

# Paleoenvironmental change in a precession-paced succession across the onset of the Messinian salinity crisis: Insight from element geochemistry and molecular fossils



Marcello Natalicchio<sup>a,\*</sup>, Francesco Dela Pierre<sup>a,\*</sup>, Daniel Birgel<sup>b</sup>, Hans Brumsack<sup>c</sup>, Giorgio Carnevale<sup>a</sup>, Rocco Gennari<sup>a</sup>, Susanne Gier<sup>d</sup>, Francesca Lozar<sup>a</sup>, Luca Pellegrino<sup>a</sup>, Mathia Sabino<sup>b</sup>, Bernhard Schnetger<sup>c</sup>, Jörn Peckmann<sup>b</sup>

<sup>a</sup> Dipartimento di Scienze della Terra, Università degli Studi di Torino, Torino, Italy

<sup>b</sup> Institut für Geologie, Centrum für Erdsystemforschung und Nachhaltigkeit, Universität Hamburg, Hamburg, Germany

<sup>c</sup> Institut für Chemie und Biologie des Meeres, Universität Oldenburg, Oldenburg, Germany

<sup>d</sup> Department für Geodynamik und Sedimentologie, Universität Wien, Wien, Austria

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## ABSTRACT

In marginal Mediterranean sub-basins, the early phase of the Messinian salinity crisis (MSC) is recorded by cyclic successions of gypsum and shales, which in deeper parts of the sub-basins make lateral transition into organic-rich shales, marls, and carbonates. The cyclic stacking pattern of the gypsum-bearing sequences is assumed to reflect periodic paleoenvironmental change induced by precession-driven climate perturbations, with the assumption that shales reflect humid climate (precession minima) while gypsum reflects arid conditions (precession maxima). However, this correlation has not been verified to date, mostly because of the scarcity of microfossils, the most commonly used tools for the reconstruction of precession-driven paleoenvironmental change. Such change can, instead, be reconstructed through the study of the deeper water counterparts of gypsum (marly and carbonate layers) with geochemical indicators (major and trace elements, molecular fossils), which provide insight on climate and aquatic productivity. We used this approach to study a section from the Piedmont Basin (NW Italy) where the onset of the MSC is archived in a sequence of organic-rich sediments. This sequence displays distinct lithological cyclicity, evidenced by the repetition of couplets of organic-rich shales and marls, either bioturbated (in the pre-MSC part of the section) or laminated (during the MSC). The influence of orbitally-driven (precession) climate oscillations is demonstrated by fluctuations of Ti/Al, Si/Al, Mg/Al, K/Al, Zr/Al, and Ba/Al ratios that are in phase with lithological cyclicity. These fluctuations are interpreted to reflect alternation of humid (shales, deposited during precession minima) and arid (bioturbated and laminated marls, deposited during precession maxima) phases, dominated by fluvial and aeolian transport of detrital material, respectively. The cyclicity of the element ratios is mirrored by changes in organic carbon content and molecular fossil inventory. In particular, the distribution of long-chain *n*-alkanes and their degree of preservation reveal that humid phases at times of precession minima were typified by the maximum input of degraded terrestrial organic matter driven by enhanced riverine runoff, which promoted water column stratification. Coeval increase in Ba content, a common paleoproductivity proxy, agrees with enhanced nutrient supply during humid periods, promoting phases of eutrophication in the basin. Lithological and geochemical changes are observed in MSC sediments deposited at times of precession maxima, evidenced by the replacement of pre-MSC bioturbated marls by laminated marls rich in filamentous fossils corresponding to the remains of probable colorless sulfide-oxidizing bacteria. Such changes reflect an intensification of water column stratification after the onset of the MSC, possibly related to the combined effect of persistent freshwater inflow and basin isolation, precluding the advent of gypsum precipitation.

\* Corresponding authors.

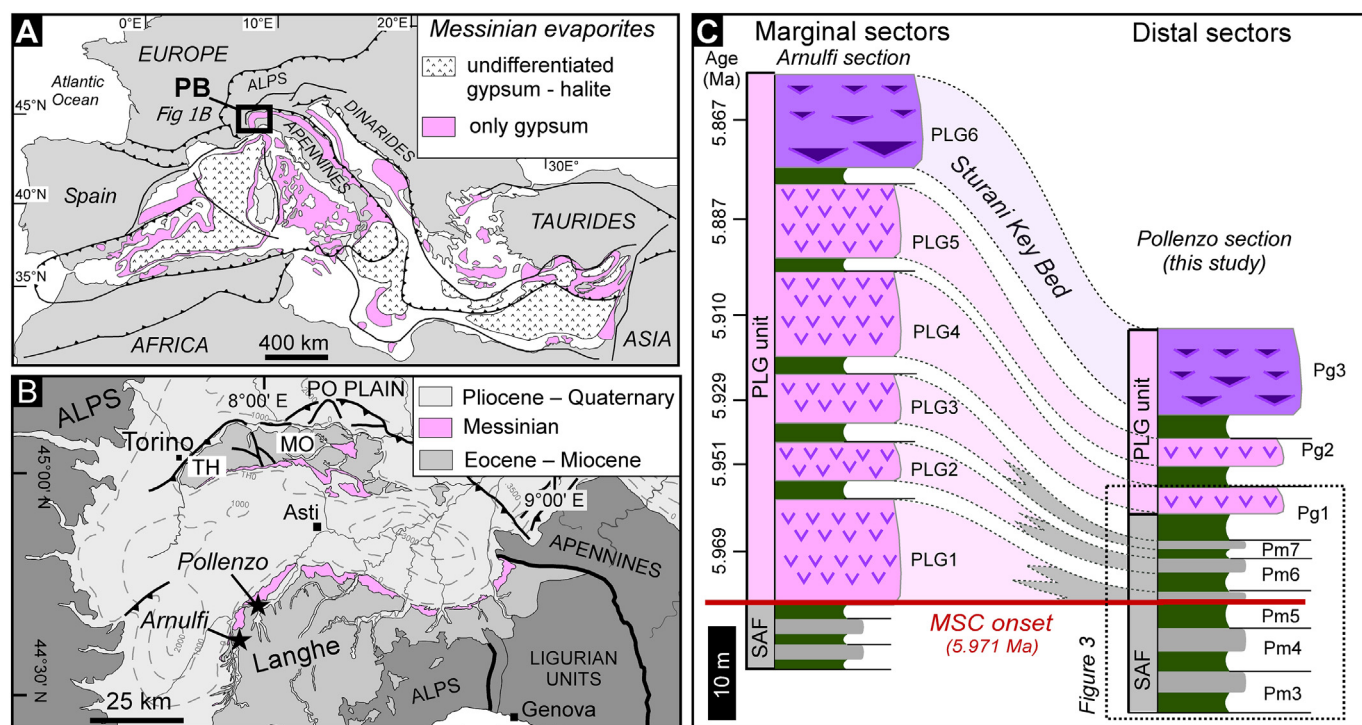
E-mail addresses: [marcello.natalicchio@unito.it](mailto:marcello.natalicchio@unito.it) (M. Natalicchio), [francesco.delapierre@unito.it](mailto:francesco.delapierre@unito.it) (F. Dela Pierre).

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**Fig. 1.** A) Distribution of the Messinian evaporites in the Mediterranean Basin (modified from Manzi et al., 2013; PB: Piedmont Basin). B) Structural sketch map of the Piedmont Basin (modified from Bigi et al., 1990). TH: Torino Hill; MO: Monferrato; gray dotted lines indicate the isobaths of the base of Pliocene. C) Sketch showing the lateral transition from marginal gypsum deposits (Primary Lower Gypsum unit; Arnulfi section) to cyclic sequences of organic-rich shales (dark gray), marls, and carbonate-rich deposits (light gray) in the deeper part of the basin (Pollenzo section). PLG: Primary Lower Gypsum; SAF: Sant'Agata Fossili marls; MSC: Messinian salinity crisis. (Modified from Dela Pierre et al., 2011). The ages of the PLG cycles are from Manzi et al. (2013).

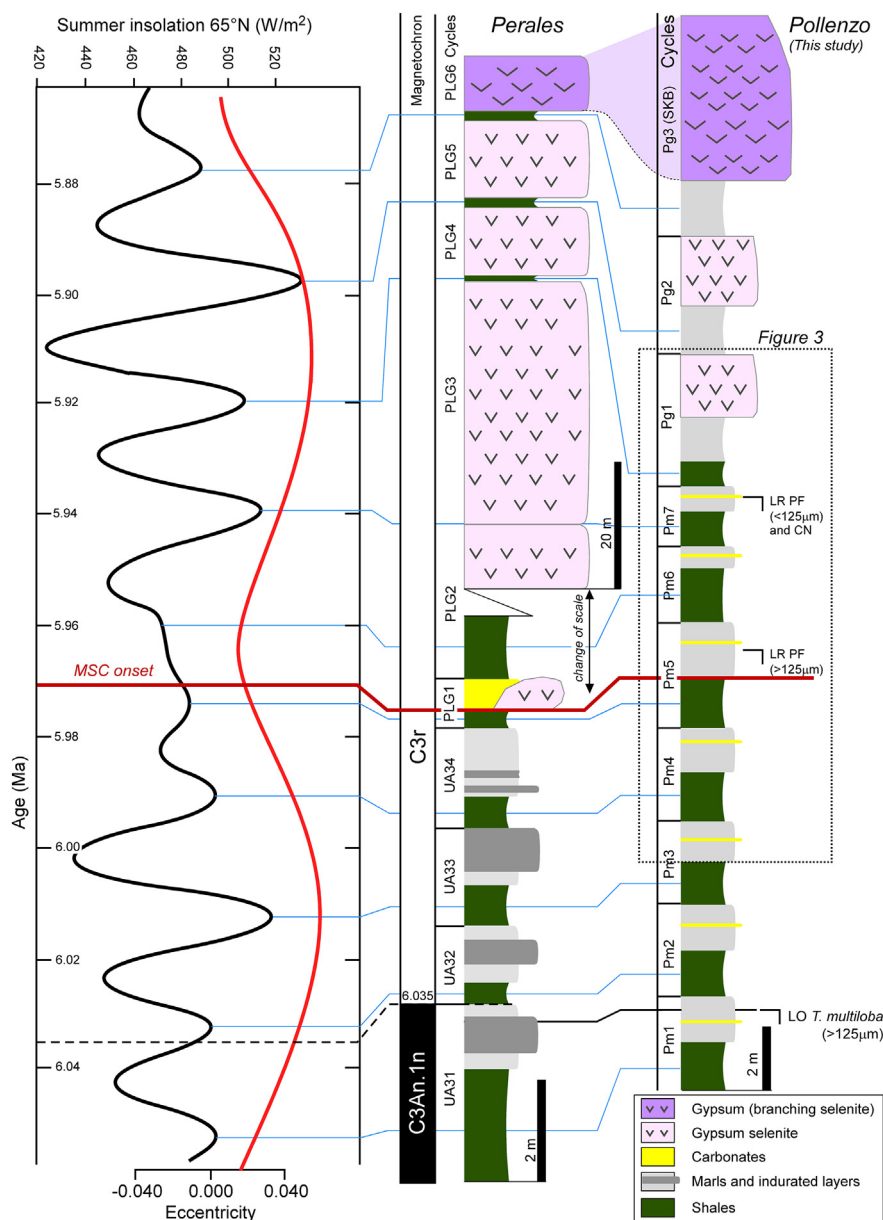
## 1. Introduction

During the Messinian, the Mediterranean Sea was progressively isolated from the Atlantic Ocean by the gradual tectonic uplift of the Betic and Rifian gateways (e.g., Duggen et al., 2003; Garcia-Castellanos and Villaseñor, 2011; Flecker et al., 2015; Capella et al., 2016). This trend was superposed to long (eccentricity) and short (precession) orbitally-driven climate perturbations, the effects of which were dramatically amplified because of limited water exchange with the Atlantic Ocean. The sedimentary products of the combined effects of tectonic restriction and astronomical forcing are cyclic successions of organic-rich shales, diatomites, and marls, deposited on the Mediterranean Sea bottom starting at about 7.1 Ma (Krijgsman et al., 1999; Negri et al., 1999; Sierro et al., 2003; Perez-Folgado et al., 2003; Kouwenhoven et al., 2006; Hilgen et al., 2007; Roveri et al., 2014; Gennari et al., 2018). The isolation of the Mediterranean culminated in the extensive deposition of evaporites during the Messinian salinity crisis (MSC; 5.97–5.33 Ma; Manzi et al., 2013), when the basin was transformed into a giant salina (Hsü et al., 1977; Cita et al., 1978; Roveri et al., 2014; Flecker et al., 2015; Fig. 1A). The onset of the MSC is considered to represent a synchronous event throughout the Mediterranean (Manzi et al., 2013). In shallow marginal sub-basins (i.e., at a paleodepth < 200 m; Roveri et al., 2014), this event is marked by the deposition of the Primary Lower Gypsum unit (Roveri et al., 2008), which is characterized by distinct lithological cyclicity defined by shale-gypsum couplets. These evaporites make lateral transition into cyclic sequences of organic-rich sediments and carbonate layers, which were deposited in basins of intermediate to deep water depths (i.e., > 200 m; Manzi et al., 2007; Dela Pierre et al., 2011, 2012; Gennari et al., 2013, 2018; Lozar et al., 2018). Apparently, the formation of gypsum in these deep water basins was hampered by bottom oxygen depletion coupled with an intense bacterial sulfate reduction, responsible for decreasing sulfate concentration and consequent undersaturation with respect to gypsum

(Babel, 2007; De Lange and Krijgsman, 2010).

Cyclic paleoenvironmental change induced by precession-driven climate perturbations have been extensively documented for pre-MSC sequences based on calcareous microfossil assemblages (e.g., Hilgen and Krijgsman, 1999; Sierro et al., 2003; Kouwenhoven et al., 2006; Gennari et al., 2018; Lozar et al., 2018) and by variations in the  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^{13}\text{C}$ , and  $\delta^{18}\text{O}$  isotope ratios of the tests of planktic foraminifers (Modestou et al., 2017; Reghizzi et al., 2017). These studies demonstrated that the formation of organic-rich shales was related to enhanced preservation of organic carbon, favored by water column stratification, bottom water stagnation and anoxia, resulting from enhanced riverine runoff at precession minima corresponding to insolation maxima. The envisioned mechanism was apparently somewhat different from that governing the deposition of the younger and more extensively studied Pliocene and Pleistocene sapropels of the Mediterranean Sea (e.g., Wehausen and Brumsack, 1998; Nijenhuis and De Lange, 2000). The latter is regarded as the product of an additional nutrient supply and enhanced productivity (Schenau et al., 1999) triggered by increased riverine runoff of the Nile caused by the northward shift of the North African monsoon system (Gladstone et al., 2007; Marzocchi et al., 2015; Rohling et al., 2015).

In contrast, the influence of precessional forcing on the deposition of the Primary Lower Gypsum unit is not straightforward, especially due to the absence or scarcity of microfossils, related to the advent of hypersaline conditions not tolerated by the majority of eukaryotes (e.g., Bellanca et al., 2001). Actually, the hypothesis of the influence of precessional forcing on evaporite deposition is only supported by lithological cyclicity to date, based on the assumption that gypsum layers reflect more arid phases during precession maxima, while shales are assumed to be indicative of humid conditions during precession minima (Roveri et al., 2014; Simon et al., 2017). One possibility to investigate the influence of precessional forcing on MSC sequences is the analysis of the deeper water equivalents of the Primary Lower Gypsum unit. Such



**Fig. 2.** Correlation of the Pollenzo section with the astronomically-tuned (65°N summer insolation and eccentricity curve; Laskar et al., 2004) Peralles reference section (Spain; modified from Manzi et al., 2013). LO: last occurrence. LR PF: last recovery of planktic foraminifers. CN: calcareous nannofossils. PLG: Primary Lower Gypsum; MSC: Messinian salinity crisis; SKB: Sturani Key Bed (modified from Lozar et al., 2018).

successions, which consist of organic-rich shales, marls, and carbonates, have received much less attention than their pre-MSC counterparts. In the absence or scarcity of body fossils, the paleoenvironmental and paleoclimatic change occurring across the onset of the MSC can be investigated in these successions through the study of inorganic and organic geochemical proxies, such as major and trace elements, providing insights on climate conditions and paleoproductivity (e.g., Wehausen and Brumsack, 1998; Calvert and Pedersen, 2007), and molecular fossils (lipid biomarkers) of terrestrial organic matter, reflecting climate-dependent change in terrestrial vegetation (e.g., Eglinton and Hamilton, 1963; Schefuß et al., 2003). We applied this approach to study an inferred precession-paced succession exposed in the Pollenzo section (Piedmont Basin, NW Italy; Figs. 1A, B) at the northernmost offshoot of the Mediterranean. In this section, the onset of the MSC does not coincide with the base of the Primary Lower Gypsum unit, but it is archived in a sequence of fine-grained sediments (organic-rich shales, marls, and carbonate rich layers; Dela Pierre et al., 2011, 2012; Violanti

et al., 2013; Lozar et al., 2018). We complemented the study of inorganic and organic geochemical proxies with sedimentological and petrographical data with the aim to monitor the mutual relationships between orbitally-driven paleoenvironmental change at the precessional scale and the production, accumulation, and final preservation of sediments and organic matter across the onset and the earliest phase of the MSC. This study provides new constraints on the physical and chemical parameters of the water column and the sedimentary environment across the onset of the MSC in a marginal basin.

## 2. The Pollenzo section

### 2.1. Geological and stratigraphical setting

The Pollenzo section (44°41'08"N; 7°55'33"E) is located in the Piedmont Basin (Fig. 1B), a wide wedge-top basin filled with Upper Eocene to Messinian sediments (Rossi et al., 2009; Mosca et al., 2010;

Rossi, 2017). The Messinian succession is exposed in the southern (Langhe) and northern (Torino Hill-Monferrato) basin margins, whereas in the depocentral zones it is buried below Pliocene and Quaternary deposits (Irace et al., 2005; Dela Pierre et al., 2011). The succession starts with outer shelf to slope deposits, referred to as the Sant'Agata Fossili Marls (Tortonian-lower Messinian; Sturani, 1973). This unit displays cyclic stacking pattern evidenced by the rhythmic repetition of shale/marl couplets (Lozar et al., 2010, 2018; Dela Pierre et al., 2011, 2012; Violanti et al., 2013). Abundance fluctuations of calcareous microfossil assemblages allowed to assign the lithological cyclicity to precessional forcing (Violanti et al., 2007, 2013; Lozar et al., 2018), with shales reflecting warm and humid conditions during precession minima (insolation maxima) and marls pointing to cool and arid climate during precession maxima (insolation minima). The Sant'Agata Fossili Marls are followed, at the basin margins, by primary sulfate evaporites of the Primary Lower Gypsum unit (Dela Pierre et al., 2011). The latter corresponds to the first stage of the MSC (5.97–5.60 Ma; Manzi et al., 2013) and consists of lithologic cycles composed of shale-gypsum couplets (Fig. 1C). No in situ primary evaporites are documented in the buried depocentral zones, but seismic data show that their time equivalent sediments are represented by shales (Irace et al., 2010).

## 2.2. Identification of the onset of the MSC

The identification of the onset of the MSC in the Pollenzo section is based on physical stratigraphic and biostratigraphic data (Dela Pierre et al., 2011; Lozar et al., 2010, 2018; Violanti et al., 2013). Physical stratigraphic correlation allowed reconstructing the lateral facies transition between the shallow marginal area of the basin and the depocentral zone; such transition is exposed on the southern sector of the Piedmont Basin (Dela Pierre et al., 2011; Fig. 1B). Along the basin margins (Arnulfi section; Figs. 1B, C), six Primary Lower Gypsum cycles were recognized, composed of bottom grown-selenite layers; the sixth bed records a sharp facies change (i.e., the appearance of the branching selenite facies; Lugli et al., 2010) and represents a distinct marker bed, referred to as the Sturani key-bed, which can be physically correlated and mapped throughout most of the Piedmont Basin (Dela Pierre et al., 2011). In the Pollenzo section, which is closer to the basin depocenter, only two gypsum beds (Pg1 and Pg2, Fig. 1C) are present below the Sturani marker bed. The Pg1 and Pg2 gypsum beds overly seven lithologic cycles (Pm1–Pm7; Fig. 2) belonging to the Sant'Agata Fossili Marls. Each cycle, about 3 m thick, is bipartite and consists of laminated organic-rich shales followed by marls, with the latter hosting a carbonate-rich bed (Dela Pierre et al., 2012). Due to their position with respect to the Sturani key-bed, the uppermost three cycles of the Sant'Agata Fossili Marls (Pm5–7) were considered as the deeper water counterparts of the lower three cycles of the Primary Lower Gypsum unit deposited in marginal sectors (Dela Pierre et al., 2011; Fig. 1C). Consequently, the onset of the MSC (i.e., the time line at 5.971 Ma) has been identified in the Pollenzo section in cycle Pm5, at the base of the marly hemicycle, which corresponds to the base of the first gypsum bed in marginal setting (Fig. 1C). Biostratigraphic data are in accord with the physical stratigraphic correlation. In cycle Pm5, Lozar et al. (2018) have documented a peculiar sequence of calcareous nannofossil bioevents (abundance peak of *Sphenolithus abies*, followed by minor peaks of *Helicosphaera carteri* and *Umbilicosphaera rotula*), as well as the disappearance of planktic foraminifers > 125 µm (*Globigerina bulloides*, *Turborotalita quinqueloba*, *Neogloquadrina* spp. *Globigerinita* spp.; Violanti et al., 2013). These bioevents are reliable tools for the identification of the onset of the MSC, independently from the occurrence of evaporites (Gennari et al., 2018; Manzi et al., 2018). Finally, an additional tie point is represented by the last occurrence of *Turborotalita multiloba* (40% of its relative abundance in the > 125 µm fraction) in the marls of cycle Pm1 (Violanti et al., 2013), which has been also recorded at the top of cycle UA31 (i.e., four cycles below the MSC

onset) in the astronomically-tuned Perales section (Sierro et al., 2001; Fig. 2).

Summarizing, four pre-MSC cycles (Pm1–Pm4) are identified in the Pollenzo section, followed by three MSC cycles (Pm5–Pm7; Fig. 2). The uppermost evaporite-free cycle (Pm7) is overlain by two gypsum-bearing cycles (Pg1 and Pg2; Figs. 1C, 2), which correspond to the 4th and 5th Primary Lower Gypsum cycles, immediately below the Sturani key-bed (6th Primary Lower Gypsum cycle; Fig. 1C).

## 3. Material and methods

A total of 57 samples were taken from cycles Pm 3, 4, 5, 6, 7, and Pg1. Each sample was split into two parts, one used for petrographical and mineralogical analyses, the other for geochemical analyses.

### 3.1. Petrography and mineralogy

The samples were cut both parallel and perpendicular to bedding after epoxy impregnation. 15 slabs and 21 thin sections from the most representative samples were studied using transmitted, reflected, and UV light microscopy. Scanning electron microscopy (SEM) analyses were performed on ten stubs for morphological analyses and on seven polished carbon-coated thin sections for semiquantitative elemental analyses and backscattered electron imagery, using a JSM-IT300LV scanning electron microscope equipped with an energy-dispersive EDS Oxford Instrument Link System microprobe (Department of Earth Sciences, University of Torino). X-ray diffraction (XRD) analyses were performed on twenty six bulk samples using a Panalytical X'Pert PRO diffractometer (CuKα radiation, 40 kV, 40 mA, step size 0.0167, 5 s per step) at the Department of Geodynamics and Sedimentology, University of Vienna. In addition, two samples representative of the main studied facies were selected for clay mineral analyses. Oriented clay samples (< 2 µm-fraction) were prepared by pipetting 1 ml of suspension (10 mg/ml) onto a glass slide. They were analyzed air-dried, saturated with Mg and K ions, and after saturation with ethylene glycol and glycerol at 60 °C for 12 h. Additionally, the samples were heated to 550 °C. The X-ray patterns were interpreted according to Moore and Reynolds (1997) and quantified using the correction factors of Schultz (1964).

### 3.2. Total carbon and CaCO<sub>3</sub> contents

49 samples were analyzed at the Institute for Geology of the University of Hamburg to determine the total organic (TOC) and inorganic (TIC) carbon contents (Table 1 and Supplementary Table 1). The samples were dried and ground with a mortar and the resulting powder split in two aliquots. The first aliquot was heated to 1350 °C and the total carbon (TC) content was measured using a LECO SC-144DR Carbon Analyzer equipped with an infrared detector. The second aliquot was heated first to 550 °C for 5 h to remove the organic carbon and then heated to 1350 °C to measure the inorganic carbon content (TIC); TOC contents were determined with the formula  $TOC = TC - TIC$ . A Synthetic Carbon Leco 502–029 ( $1.01 \pm 0.02$  carbon%) standard was measured prior to sample analyses. To express the TIC as percent calcium carbonate (CaCO<sub>3</sub>), the following calculation was made:  $CaCO_3 = TIC \times 8.33$ .

### 3.3. X-ray fluorescence analyses (XRF)

49 samples were analyzed using fused glass beads for major (Al, Si, Mg, K, Ti) and trace (Ba, Zr) elements using a wavelength-dispersive XRF spectrometer (Axios max®, Panalytical) at the Institute of Chemistry and Biology of the Marine Environment (University of Oldenburg). Analytical accuracy was checked with an in-house black shale reference material and international standard and was better than 1% for major elements and 5% for trace elements. The results are



**Table 1**Average geochemical data (TOC, CaCO<sub>3</sub>, major and trace elements) of the Pollenzo section samples.

	Shales	Bioturbated marls	Laminated marls
TOC (wt%)	1.98	1.40	2.09
CaCO <sub>3</sub> (%)	18.3	33.8	34.8
XRF analyses			
SiO <sub>2</sub> (%)	41.3	35.1	30.0
Al <sub>2</sub> O <sub>3</sub> (%)	13.0	10.3	9.0
MgO (%)	4.8	4.8	7.7
CaO (%)	12.4	19.9	20.1
Na <sub>2</sub> O (%)	0.8	0.7	0.7
K <sub>2</sub> O (%)	2.6	2.1	1.9
Ti <sub>2</sub> O (%)	0.5	0.4	0.4
Ba (ppm)	604	296	248
Zr (ppm)	80	84	83
Ratios			
Ti/Al × 100	4.55	4.80	4.87
Mg/Al × 100	43.91	55.46	107.25
Si/Al	2.81	3.00	2.96
K/Al × 100	31.29	32.59	32.34
Zr/Al	11.67	16.15	19.94
Ba/Al	87.26	54.48	62.33
No. of samples	21	16	12

shown in Table 1 and Supplementary Table 1. Redox-sensitive elements (e.g., Mo and U; Algeo and Tribouillard, 2009) have also been analyzed, but only low contents close to detection limit were obtained, lacking distinct patterns. We, therefore, decided not to use these data. Because of the high concentration of Al in aluminosilicates, element/Al ratios were used for the assessment of the relative enrichment or depletion of specific elements in the samples (e.g., Brumsack, 2006; Calvert and Pedersen, 2007).

### 3.4. Molecular fossils

The detailed cleaning and extraction procedure applied in this study has been reported elsewhere (Birgel et al., 2006). A total of 42 dry sediment samples were homogenized by mortar and pestle. The muddy sediments were first saponified with 6% potassium hydroxide in methanol using an ultrasonic bath to release carboxylic acids (2 h at 80 °C). The saponification extract was collected in a separatory funnel. Then, the samples were extracted by ultrasonication with dichloromethane (DCM):methanol (3:1). This procedure was repeated until the extract became colorless. The combined extracts were treated with 10% hydrochloric acid to pH 1 to transfer the free fatty acids to the organic solvent phase. For gas chromatography (GC) analysis, each extract was cleaned by separation into *n*-hexane soluble and DCM soluble fractions. The *n*-hexane fraction was further treated and separated via solid phase extraction using a Supelco glass cartridge (6 ml, 500 mg, DSC-NH2) into four fractions of increasing polarity: (1) hydrocarbons with 4 ml *n*-hexane, (2) ketones with 6 ml *n*-hexane:DCM (3:1, v/v), (3) alcohols with 7 ml DCM:acetone (9:1, v/v), (4) carboxylic acids with 8 ml 2% formic acid in DCM. Alcohols were derivatized to trimethyl silyl ethers by reacting them with a 1:1 mixture of pyridine and *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) at 70 °C for 60 min. Free carboxylic acids were reacted with 1 ml 14% boron trifluoride in methanol at 70 °C for 1 h to form fatty acid methyl esters. After cooling, the mixture was extracted four times with 2 ml *n*-hexane. Combined extracts were evaporated under a stream of nitrogen, and redissolved in *n*-hexane prior injection. The hydrocarbon fraction, the derivatized alcohol and carboxylic acid fractions were analyzed using coupled gas chromatography–mass spectrometry (GC–MS) with a Thermo Scientific Trace GC Ultra coupled to a Thermo Scientific DSQ II mass spectrometer. Quantification was performed using GC-flame ionization detection (GC-FID) with a Fisons Instruments GC 8000. Internal standards used were 5 $\alpha$ -cholestane for hydrocarbons, 1-nonadecanol and DAGE *n*-

C<sub>18</sub>/*n*-C<sub>18</sub> for the alcohols, and 2-Me-C<sub>18</sub> fatty acid for the carboxylic acids. Both GC systems were equipped with a HP-5 MS UI fused silica column (30 m × 0.25 mm i.d., 0.25  $\mu$ m film thickness). The carrier gas was helium for the GC–MS measurements and hydrogen for the GC–FID measurements. The GC temperature program for all fractions was: 50 °C (3 min); from 50 °C to 230 °C (held for 3 min) at 25 °C/min; from 230 °C to 325 °C (held 20 min) at 6 °C/min. Compound assignment was based on retention times and published mass spectral data.

Compound-specific carbon isotope analyses of all *n*-alkanes were performed with an Agilent 6890 gas chromatograph coupled with a Thermo Finnigan Combustion III interface to a Thermo Finnigan Delta Plus XL isotope ratio mass spectrometer (GC–IRMS) at the Institute for Geology, University of Hamburg. The GC conditions were identical to those mentioned above for GC–FID and GC–MS analyses. Compound-specific carbon isotope values are given as  $\delta^{13}\text{C}$  values in per mil (‰) relative to the Vienna Pee Dee Belemnite (V-PDB).

#### 3.4.1. Lipid-based ratios

The Carbon Preference Index (CPI) was calculated for *n*-alkanes according to the formula below (Bray and Evans, 1961). It represents the predominance of odd over even *n*-alkanes of a certain length range.

$$\text{CPI} = 0.5 \times \left( \frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{24} + C_{26} + C_{28} + C_{30} + C_{32}} + \frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{26} + C_{28} + C_{30} + C_{32} + C_{34}} \right) \quad (1)$$

The CPI for *n*-alkanes is a measure of the freshness of terrestrial organic matter. During biosynthesis, higher plants produce odd-numbered long chain *n*-alkanes, but subsequent diagenesis (or a change in the source) leads to homogenization of the distribution (e.g., Eglinton and Hamilton, 1967; Schefuß et al., 2003; Pancost and Boot, 2004). Consequently high CPI values indicate a good preservation of organic matter, whereas low CPI values (~1) suggest its increased degradation (e.g., Schefuß et al., 2003; Jeng, 2006).

The average chain length (ACL) was calculated for *n*-alkanes with the formula (modified from Poynter and Eglinton, 1990):

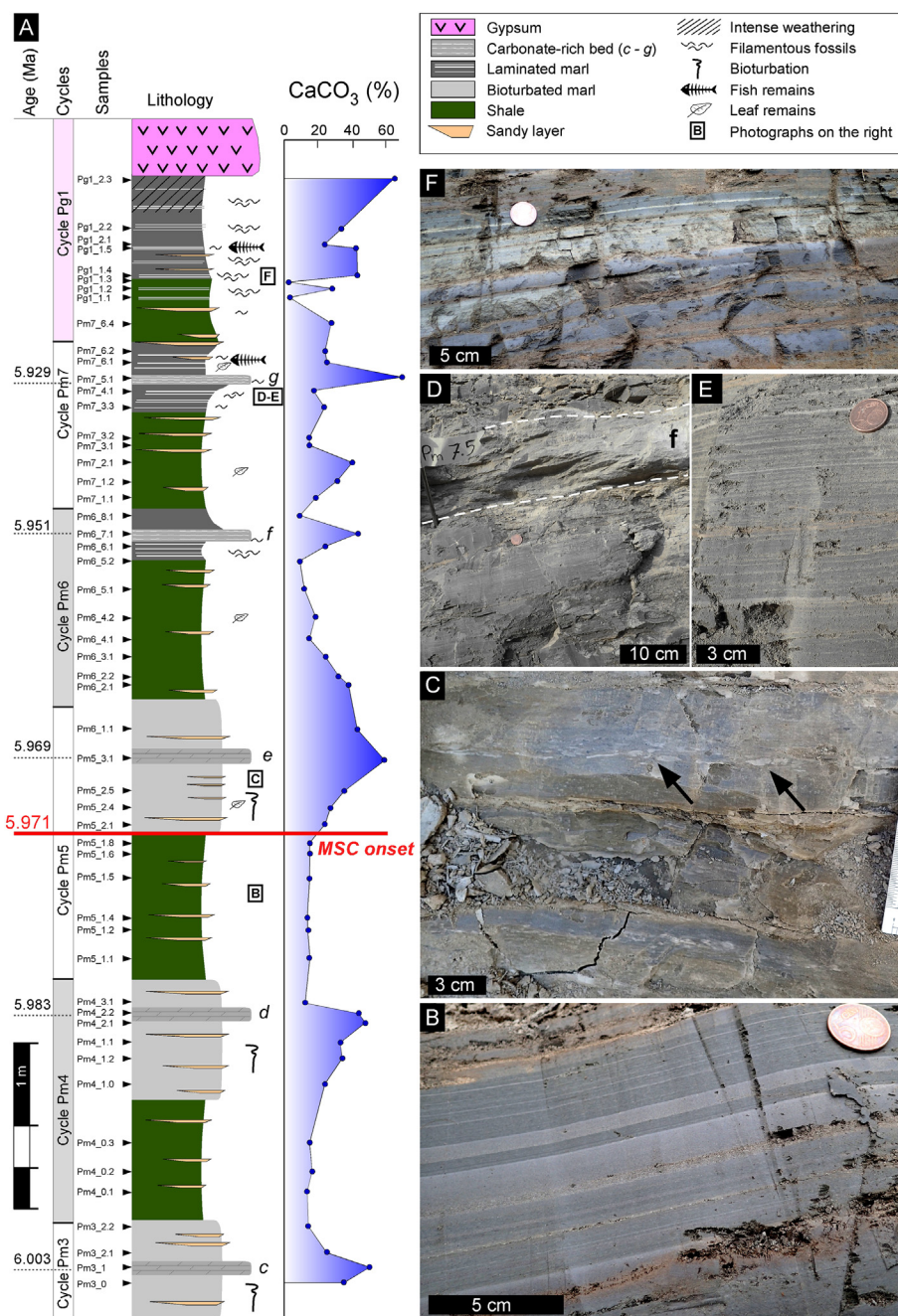
$$\text{ACL} = \frac{25 \times C_{25} + 27 \times C_{27} + 29 \times C_{29} + 31 \times C_{31} + 33 \times C_{33}}{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}} \quad (2)$$

The *n*-C<sub>35</sub>-alkane was excluded from the formula because of the co-elution with lycopane, a biomarker whose provenance is still under discussion (Sinninghe Sinninghe Damsté et al., 2003; Wakeham et al., 2007). The ACL index is commonly used to monitor changes in long chain *n*-alkane distribution and to identify changes in the sources of higher plant-derived *n*-alkanes (Bush and McInerney, 2015; Diefendorf and Freimuth, 2017; Eley and Hren, 2018).

## 4. Results

### 4.1. Petrography and mineralogy

The lithological cyclicity of the Pollenzo section is evidenced by the rhythmic repetition of shales and bioturbated marls in cycles Pm3, 4, and 5 and of shales and laminated marls in cycles Pm6 and Pm7 (Fig. 3). These lithological variations are reflected by fluctuations in calcium carbonate contents, with average contents < 20% in the shales, > 30% in the bioturbated marls, and ranging from 20 to 60% in the laminated marls (Table 1, Fig. 3A). High calcium carbonate contents were found in the shales of cycle Pm6 due to the presence of aragonite-rich laminae (confirmed by XRD analyses), and in cycle Pg1 due to the presence of dolomite (see below). The bioturbated and laminated marls of each cycles host an indurated carbonate-rich bed (with calcium carbonate contents ranging from 43% to 68%). Petrographic features of these beds have been reported in Dela Pierre et al. (2012).



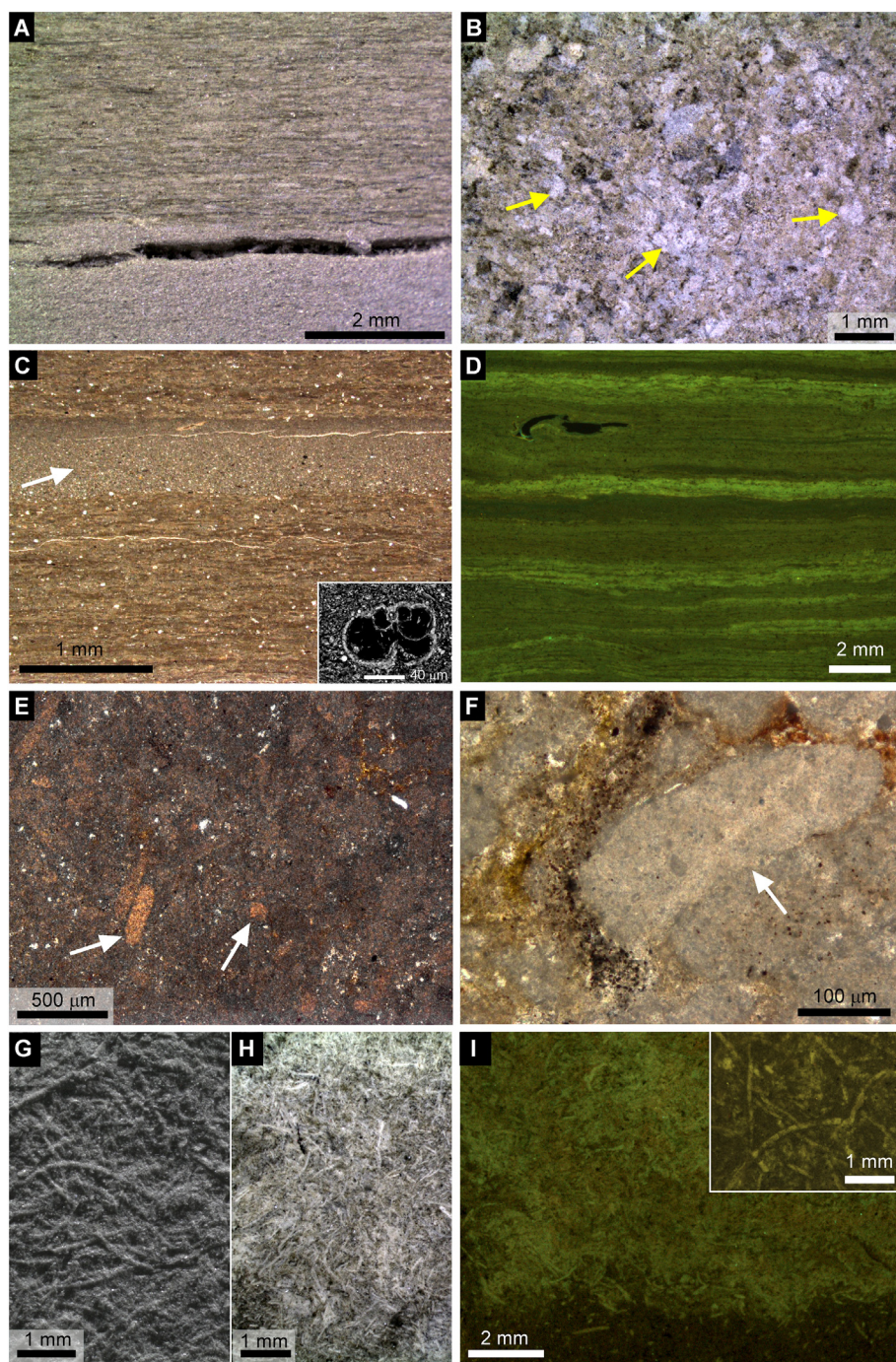
**Fig. 3.** A) The Pollenzo section, with locations of the studied samples and their corresponding calcium carbonate (CaCO<sub>3</sub>) contents. B) Outcrop view of the shales of cycle Pm5: olive gray, laminated shales are interbedded with light gray silty layers, locally showing normal grading. C) Bioturbated marls of cycle Pm5; burrows are indicated by arrows. D) Laminated marls of cycle Pm7, hosting a carbonate-rich bed (f). E) Detail of D, showing fine lamination, defined by alternation of gray and whitish laminae. F) Laminated beds including a whitish layer of cycle Pg1. The ages of cycles are from Manzi et al. (2013).

The lower part of both the pre-MSL and MSL cycles consists of finely laminated olive to gray shales, representing organic-rich shales with high TOC contents (1.5–2%, see below; Fig. 3B). These sediments are irregularly interbedded with cm-thick sandy and silty layers interpreted as the product of high energy fluvial floods (Dela Pierre et al., 2014; Figs. 3B, 4C). Lamination is defined by the alternation of sub-mm thick dark terrigenous laminae and whitish laminae (Fig. 4A), which mostly consist of fluorescent peloids (Fig. 4D). Two types of peloids were recognized: (1) irregular aggregates up to 300 µm across (Fig. 4B), which are composed of silt-sized terrigenous grains, clay, and altered diatom frustules (Fig. 5A), particularly abundant in cycles Pm6 and 7; (2) fecal pellets, up to 0.5 mm across and with an average length of a few mm, characterized by a distinct ovoid or subcylindrical shape

(Fig. 4E, F). These pellets are composed of a mixture of siliciclastic grains and monospecific assemblages of coccoliths, especially in cycles Pm5 and Pm6 (Fig. 5B). The coccoliths are engulfed in amorphous silica, most likely derived from the dissolution of diatoms. Other components are planktic foraminifers (*Orbulina universa*, *Globigerina bulloides*, *Globigerinita* spp., *Globigerinoides* spp. and *Globoturbotalita apertura* gr.), the abundance of which decrease dramatically in the MSL cycles, where only specimens smaller than 125 µm (*Turbotalita quinqueloba*, *Globigerinita* spp., *Neoglobobadrina* spp.) have been recorded (Fig. 4C; Violanti et al., 2013). Pyrite framboids are abundant (inset Fig. 5C). Their small size, ranging from 3 to 7 µm, suggests a possible origin within the water column (Wilkin et al., 1996).

Gray, strongly bioturbated marls characterize the upper part of





**Fig. 4.** A) Polished slab cut perpendicular to bedding of shales of cycle Pm6: note lamination defined by alternation of whitish and darker laminae; a massive silty layer is present in the lower part of the image. B) Polished slab of a whitish lamina cut parallel to bedding from the layer shown in A); note the irregularly-shaped whitish aggregates, probably corresponding to marine “snow” floccules (arrows). C, D) Photomicrographs in transmitted (C) and UV light (D) of the shales of cycle Pm6. Note the graded, terrigenous layer (arrow) in (C) and the bright, organic-rich laminae rich in peloids in (D). The dark elongated clast in the upper left corresponds to a phosphatic fish remain. The inset in (C) is a back-scatter SEM image of a dwarf planktic foraminifer (sample Pm6\_4.2). E), F) Photomicrographs in transmitted light of fecal pellets (arrows) in the shale of cycle Pm7. G), H) Slabs cut parallel to bedding (G fresh cut; H polished slab) of the laminated marls of cycles Pm6 and Pg1, showing dense mazes of filamentous microfossils. I) UV light photomicrograph of the laminated marls, with autofluorescent filamentous microfossils. Detail with enlarged filaments is shown in the inset.

cycles Pm3, Pm4, and Pm5 (Fig. 3C). Apart from benthic foraminifers, which are particularly abundant in cycles Pm3 and Pm4, the marls are rich in silt-sized detrital grains, mostly quartz and mica flakes. Planktic foraminifers are scarce (Violanti et al., 2013).

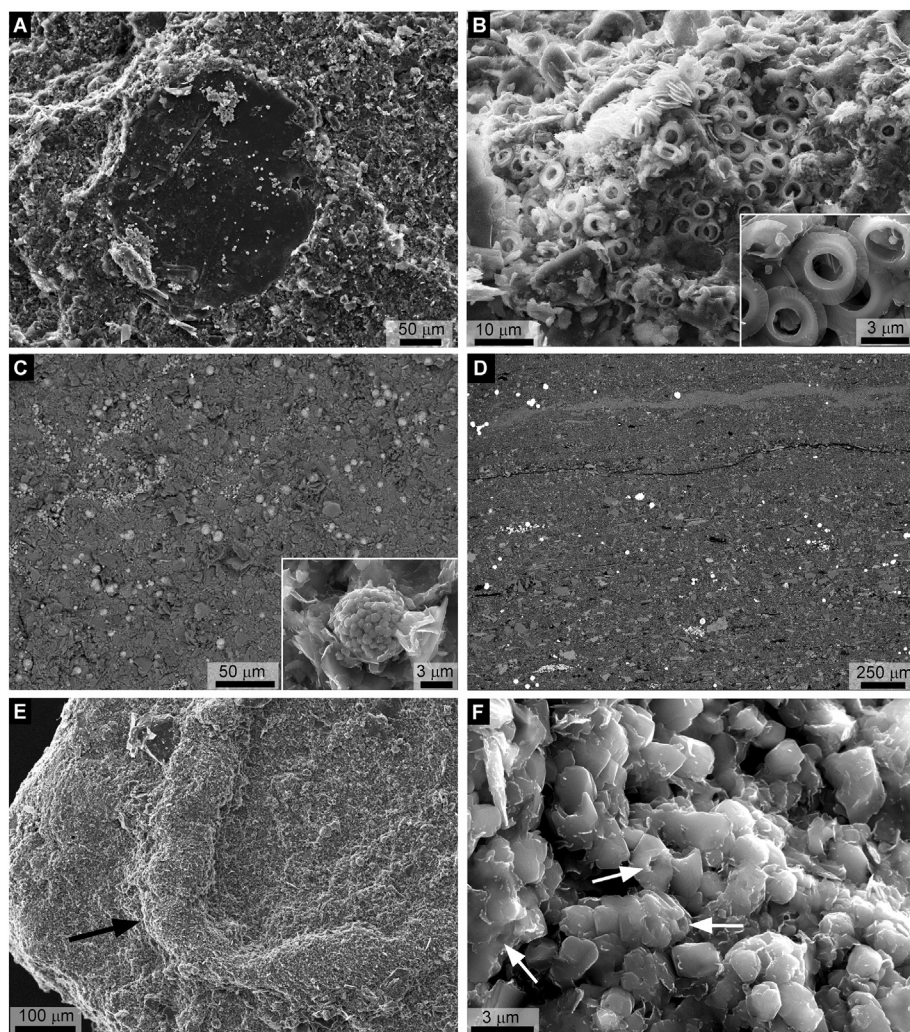
Organic carbon-rich laminated marls (TOC content > 2%, see below) form the upper part of cycles Pm6 and Pm7 and are also found in cycle Pg1 just below the gypsum. The lamination is defined by an alternation of terrigenous-rich gray laminae and whitish laminae (Figs. 3D, E, 5D). The latter are rich in fluorescent curved and straight filaments, up to 70  $\mu\text{m}$  across and several mm long (Figs. 4G, H, I and 5E), which commonly contain micron-sized iron sulfide grains. These filaments, also observed in indurated beds f and g, have been attributed to fossil colorless sulfide-oxidizing bacteria like *Beggiatoa* or *Thioploca* (see Dela Pierre et al., 2012, 2014), and apparently correspond to the

filamentous fossils found in Messinian gypsum (Dela Pierre et al., 2015). In cycles Pm7 and Pg1, the filaments are coated by spheroidal dolomite microcrystals with a hollow core (Fig. 5F) of probable microbial origin (cf. Lindtke et al., 2011) and are found in well laminated whitish layers (Fig. 3F). Rare, small sized foraminifers (< 125  $\mu\text{m}$ ) and calcareous nannofossils are present up to cycle Pm7 (Violanti et al., 2013).

#### 4.2. Element and Total Organic Carbon (TOC) fluctuations

The Si/Al, Ti/Al, K/Al, Mg/Al, and Zr/Al ratios display a cyclical trend in phase with lithological cyclicity (Fig. 6; Supplementary Table 1), with lower ratios in shales and higher values in bioturbated marls and especially in the filament-bearing laminated marls of cycles





**Fig. 5.** A) Back scatter SEM image of a mold of a centric diatom in the shales of cycle Pm6. B) SEM image of a fecal pellet composed of coccoliths engulfed in a silica-rich matrix (cycle Pm5). Detail in the inset. C) Back scatter SEM image of the shales of cycle Pm6; the light grains are pyrite framboids. Detail of a framboid is shown in the inset. D) Back scatter SEM image of the laminated marls of cycle Pm6, showing the contact between laminae rich (below) and poor (above) in terrigenous particles. E) SEM image of a curved filament (arrow) from the laminated marls of cycle Pg1. F) SEM image of roundish dolomite microcrystals on the outer surface of a filamentous microfossil. Some crystals display a hollow core (arrows).

Pm6, Pm7, and Pg1. In cycle Pg1, anomalously high Mg/Al ratios were obtained, which most likely are related to abundant dolomite microcrystals (Figs. 5F, 6). The Ba/Al ratio reveals a cyclic pattern too, but covaries negatively with the Ti/Al, Si/Al, K/Al, Mg/Al, and Zr/Al ratios, being higher in the shales and lower in the bioturbated and laminated marls (Fig. 6).

The TOC contents in the pre-MSC deposits (cycles Pm3 and Pm4) follow the lithological cyclicity and are higher in the shales (mean values ~2.0%) than in the bioturbated marls (mean values ~1.4%; Fig. 7). In the MSC deposits, however, highest TOC contents were observed in the laminated marls from cycles Pm6, Pm7 (values > 2%), and especially Pg1 (values up to 3.3%).

#### 4.3. Molecular fossils: *n*-alkane distribution, ratios and stable carbon isotope composition

The *n*-alkane chain lengths vary between  $C_{15}$  and  $C_{37}$  with the predominance of odd chain lengths from  $C_{29}$  to  $C_{33}$  *n*-alkanes (Fig. 8). The average chain length (ACL) shows a slight upward decrease from cycle Pm4 (ACL = 29.7) to Pm6 (ACL = 29.1), whereas the values increase in cycle Pg1 to 29.8 (Fig. 6). Among the short chain *n*-alkanes, the most abundant chains are  $C_{19}$  to  $C_{21}$  with contents ranging from ~1  $\mu\text{g/g}$  TOC in the bioturbated and laminated marls to ~12  $\mu\text{g/g}$  TOC (cycle Pm6) in the shales. The long chain ( $C_{29}$ – $C_{33}$ ) *n*-alkane abundances show the same cyclic fluctuation with minimum contents in the marls (~20  $\mu\text{g/g}$  TOC in cycle Pg1) and maximum contents in the shales (up to 236  $\mu\text{g/g}$  TOC in cycle Pm5; see Fig. 7, Table 2 and

Supplementary Table 2).

The CPI of *n*-alkanes (CPI) ranges from 2 to 9 (Fig. 7). A negative correlation between the CPI and the *n*-alkane contents is evident, with lower CPI values (~2–6) observed in the shales and slightly higher CPI values (up to 9) in the bioturbated and laminated marls.

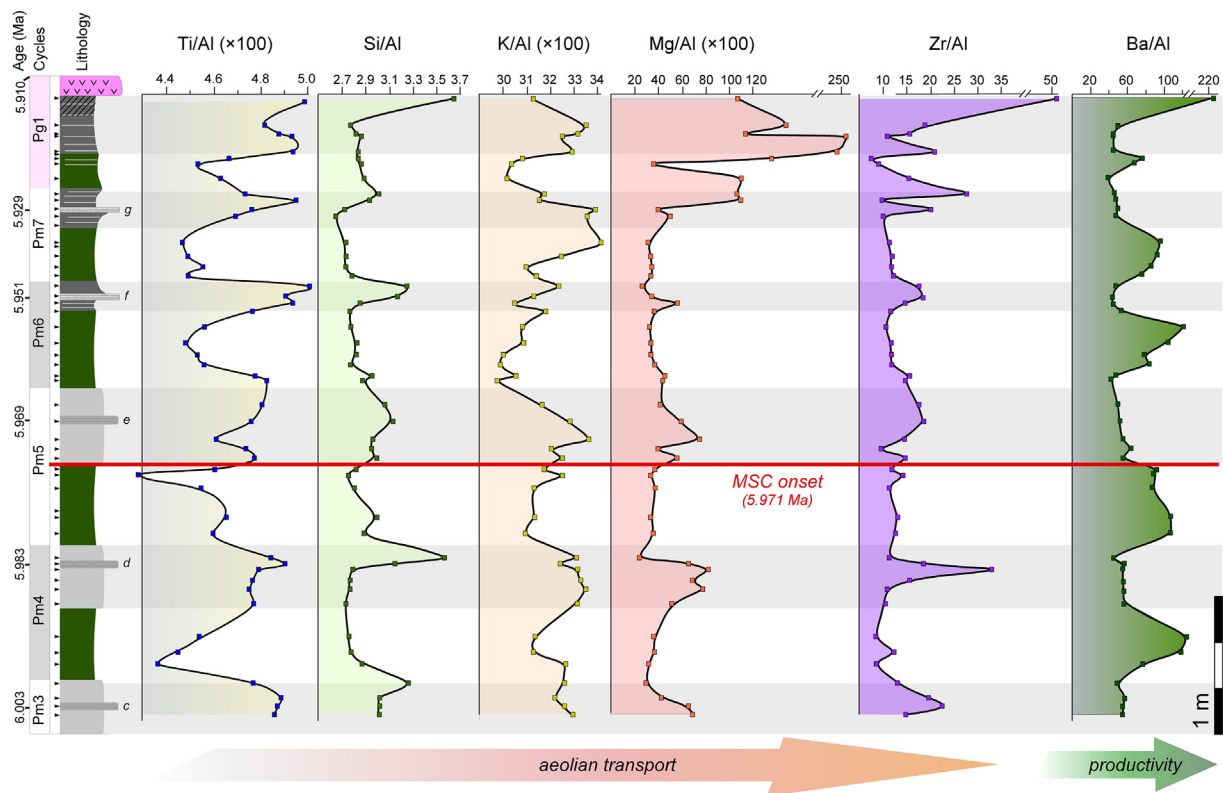
The  $\delta^{13}\text{C}$  values of long chain *n*-alkanes ( $C_{29}$ – $C_{33}$ ) range from –36‰ to –29‰ (Figs. 7, 9 and Supplementary Table 2). The bioturbated and laminated marls, but especially the carbonate layers are typified by low  $\delta^{13}\text{C}$  values. A trend towards lower  $\delta^{13}\text{C}$  values is observed across the onset of the MSC from cycle Pm4 to Pm6. In cycles Pm7 and Pg1, a trend towards higher values is observed. Apart from these trends, the shales are generally characterized by higher  $\delta^{13}\text{C}$  values, with positive shifts up to ~8‰ in comparison with the bioturbated and laminated marls.

## 5. Discussion

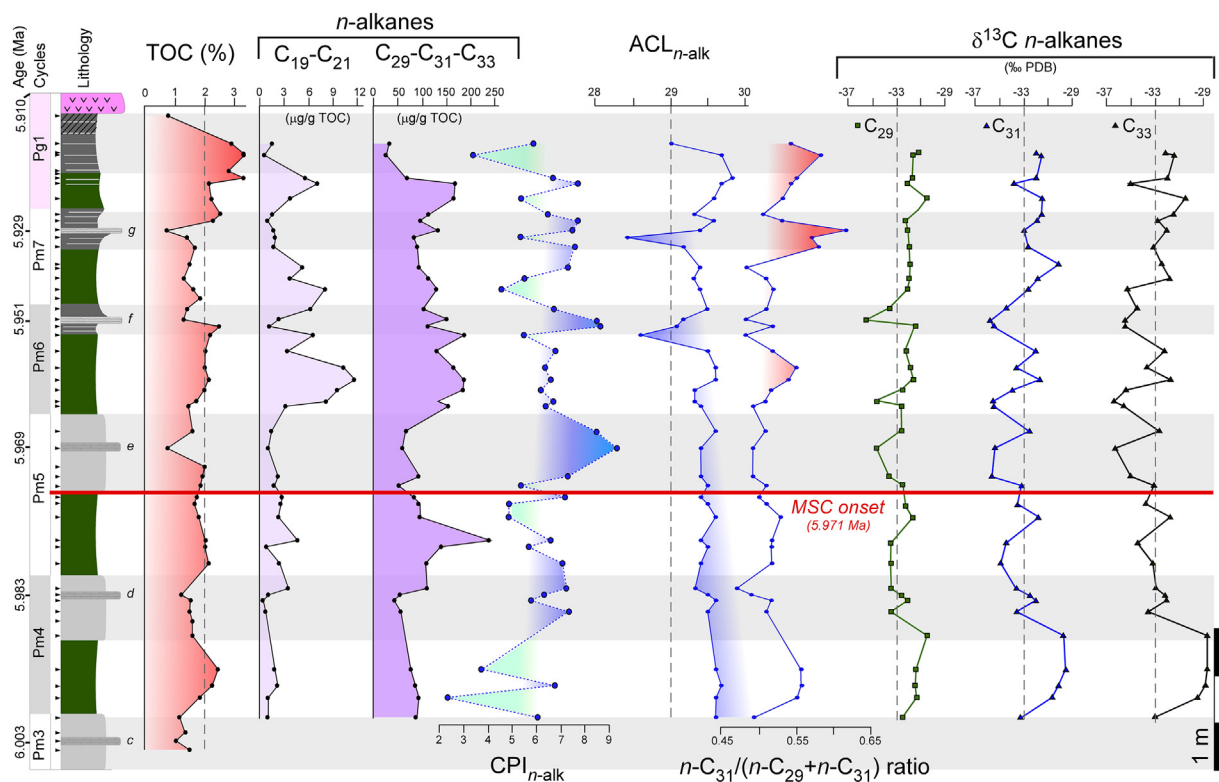
### 5.1. Fluctuations of element abundances and insights on the provenance of the fine-grained detrital fraction

The chemical composition of the Pollenzo sediments provides information on climate by identifying specific sedimentary components that have been transported to the basin by aeolian or fluvial processes during dry and wet climatic periods, respectively (e.g., Wehausen and Brumsack, 2000; Martinez-Ruiz et al., 2000; Calvert and Pedersen, 2007). In particular, Ti/Al, Si/Al, and Zr/Al ratios are used to track aeolian transport. Titanium is enriched compared to Al in soils during

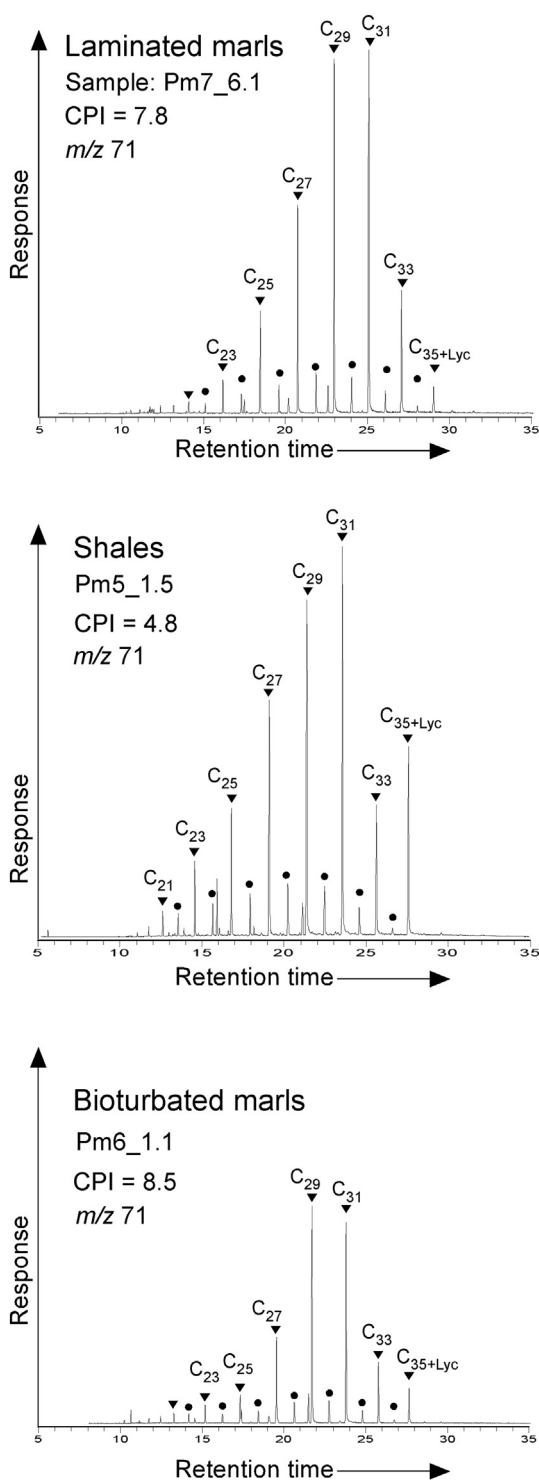




**Fig. 6.** Element/aluminum (Al) ratios of the Pollenzo section. Gray shaded bars indicate bioturbated and laminated marls. For key to lithologies see Fig. 3. The ages of cycles are from Manzi et al. (2013).



**Fig. 7.** TOC (%) content, *n*-alkane distribution (μg/g TOC), ratios of *n*-alkanes (ACL), and compound-specific carbon isotope values (δ<sup>13</sup>C) of specific *n*-alkanes of the Pollenzo section. Gray shaded bars indicate bioturbated and laminated marls. alk: alkanes; CPI: Carbon Preference Index; ACL: Average Chain Length. For key to lithologies see Fig. 3. The ages of cycles are from Manzi et al. (2013).



**Fig. 8.** Gas chromatograms ( $m/z$  71) of  $n$ -alkanes from three selected samples of laminated marls (top), shales (center), and bioturbated marls (bottom). Black triangles:  $n$ -alkanes with odd carbon numbers; black dots:  $n$ -alkanes with even carbon numbers. Note that the shale sample (Pm5\_1.5) contains more  $n$ -alkanes with even carbon number than the other lithologies (marls), resulting in a lower CPI (Carbon Preference Index) value. C<sub>35</sub>-Lyc: coelution of  $n$ -C<sub>35</sub>-alkane and lycopane.

phases of intense chemical weathering and is wind transported in the detrital silt-sized fraction as rutile, titanite, and other Ti-rich minerals during arid phases (Moller et al., 2012; van der Laan et al., 2012). In contrast, the Ti/Al ratio drops during humid phases, when the denser vegetation cover decreases the deflation potential of the surface (e.g.,

**Table 2**

Average molecular fossil abundances (alk = alkane).

	Shales	Bioturbated marls	Laminated marls
$\Sigma n\text{-C}_{29-33}$ alk ( $\mu\text{g/g}$ TOC)	126.3	68.9	95.3
$\Sigma n\text{-C}_{19-21}$ alk ( $\mu\text{g/g}$ TOC)	4.6	1.5	2.0
No. of samples	24	9	9

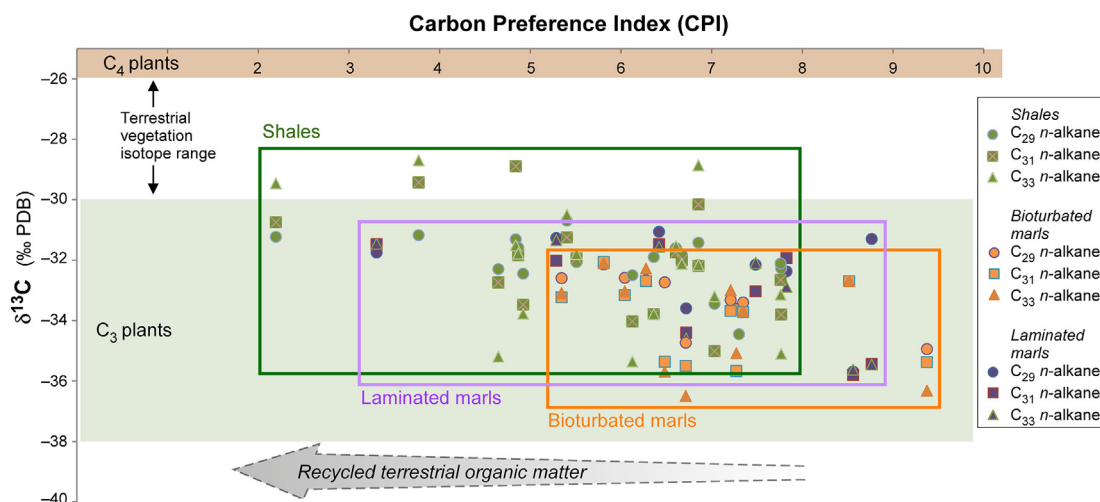
Moller et al., 2012). Silicon and Zr are mostly sourced by quartz and zircon, respectively; these minerals are very resistant to weathering and are enriched in aeolian dust (Schnetger, 1992).

In the Pollenzo section, the fluctuations of element abundances display an excellent correlation with the lithological cyclicity in both the pre-MSC and MSC cycles (Fig. 6). The high Ti/Al, Zr/Al, and Si/Al ratios observed in the bioturbated (cycles Pm3, 4 and 5) and filament-bearing laminated marls (cycles Pm6 and Pm7 and Pg1) reflect arid climate and predominant aeolian transport of the detrital fraction. The low element/Al ratios (Figs. 6, 10A, B) in the shales on the other hand point to an increase in riverine transport during more humid climatic conditions. Interestingly, in the first gypsum bearing cycle (Pg1), the onset of the arid phase does not coincide with deposition of gypsum, as commonly assumed (e.g., Krijgsman et al., 2001; Lugli et al., 2010; Manzi et al., 2013); rather a sharp increase of the Ti/Al ratio is observed approximately 1 m below the gypsum, coinciding with the appearance of the laminated marls (Fig. 5).

Additional information is provided by K/Al and Mg/Al ratios (Figs. 6, 10C). These ratios reflect the composition of clay minerals transported to the basin (Calvert and Pedersen, 2007). Low K/Al and Mg/Al ratios indicate a predominance of K- and Mg-poor clay minerals such as those of the smectite group. In the northern Adriatic Sea, smectite-rich sediments are currently supplied by the Po River and tributary rivers draining the Alpine and the Apennines catchment areas (Boldrin et al., 1988). Smectite minerals are especially abundant (around 20% of the overall clay minerals) in Mediterranean Pliocene sapropels from the Levantine (e.g., IODP site 967) and the Ionian basins (IODP site 964; Foucault and Mélières, 2000), where they are regarded to be mostly sourced from the Nile river or from rivers of the northern borderland of the eastern Mediterranean (Wehausen and Brumsack, 2000; Hamann et al., 2009; Zhao et al., 2016), respectively. In contrast, high K/Al and Mg/Al ratios indicate a greater contribution of illite (K-rich) and chlorite (Mg-rich), which are common components of aeolian dusts (Tomadin et al., 1984; Tomadin and Lenaz, 1989; Wehausen and Brumsack, 2000; Hamann et al., 2009). However, these ratios alone should only be used with caution, since lower amounts of illite and chlorite can also be supplied by rivers (Tomadin, 2000); in the northern Mediterranean Sea these minerals are supplied by rivers draining the Alpine metamorphic basement (Foucault and Mélières, 2000). Therefore, their use for paleoclimate and provenance reconstructions needs to be validated by other proxies like the Ti/Al ratio and the distribution of terrestrial-sourced molecular fossils (e.g.,  $n$ -alkanes).

In the case of the Pollenzo section, in both the pre-MSC and MSC shales the K/Al and Mg/Al ratios are lower than in the bioturbated and laminated marls (Fig. 10C). Such a pattern is in agreement with the clay mineralogy data, indicating the predominance of smectite (~47%) in the shales of cycle Pm6 (sample Pm6\_4.1; Fig. 11) and suggests that the detrital clay fraction was mostly supplied by rivers during more humid phases. Interestingly, the Al<sub>2</sub>O<sub>3</sub> contents of the Pollenzo sediments fall between the range of Pleistocene and modern fluvial sediments transported by the Po River, whose main catchment area is the Alpine chain (Amorosi et al., 2002; Fig. 10A). This observation confirms that the detrital material in the Piedmont Basin had a regional origin from the neighboring Alpine domains in agreement with the inferred accelerated denudation of the south-westernmost sector of the Alps between 7 and 5 Ma (Foeken et al., 2003; Carrapa and Garcia-Castellanos, 2005; Willet et al., 2006).





**Fig. 9.** Plot of the carbon preference index (CPI) and  $n$ -C<sub>29–33</sub> alkane  $\delta^{13}\text{C}$  values. The green, purple, and orange rectangles enclose clusters of shale, laminated, and bioturbated marl samples, respectively. Green and light brown shades indicate the range of  $\delta^{13}\text{C}$  values of C<sub>3</sub> and C<sub>4</sub> plants, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The K/Al and Mg/Al ratios of bioturbated marls (cycles Pm3–Pm5) and laminated marls of cycle Pm6 are higher than those of shales, confirming – along with the higher Ti/Al and Zr/Al ratios – the prominent role of aeolian transport (Fig. 10A, B). However, the total Al content of marls is only slightly lower than that of shales, which points to the persistence of riverine input of detrital material even during more arid phases (Figs. 10A, B). The apparent coexistence of aeolian and fluvial transport during dryer conditions is further confirmed by the clay mineral assemblage in the bioturbated marls of cycle Pm6 (sample Pm6.1.1; Fig. 11), reflecting similar amounts of riverine smectite and aeolian illite. Interestingly, palygorskite is absent and kaolinite is scarce in marls (6%). Since these minerals are typical components of Saharan dusts (Foucault and Mélières, 2000; Zhao et al., 2016; Ehrmann et al., 2017), an African origin of aeolian material is unlikely for the Pollenzo section. The predominance of illite and chlorite is rather consistent with a northern provenance of aeolian dust. These minerals are abundant in dust sourced from the North today (i.e. the European hinterland), and their contents decrease southward (Tomadin et al., 1984; Tomadin and Lenaz, 1989). A slight change in the ratio of fluvial to aeolian transport is possibly recorded in the laminated marls of cycles Pm7 and Pg1 prior to the first occurrence of gypsum in the Pollenzo section. Although the Mg/Al ratio is compromised by the presence of dolomite, the increased Ti/Al and Zr/Al ratios and the overall decrease of Al contents indicate relatively less riverine input (Figs. 10A, B).

Based on calcareous microfossil assemblages, such oscillations between humid and arid phases have already been described for the pre-MSC cycles of the Pollenzo section (Lozar et al., 2018) and other Mediterranean sections (Sierro et al., 2001, 2003; Kouwenhoven et al., 2006; Gennari et al., 2018). The data presented here reveal that variations in element abundance in the microfossil-poor cycles of the MSC follow the same trends as in the pre-MSC cycles. Our new data provide for the first time independent evidence that lithological cyclicity during the early stage of the MSC was controlled by precession-driven changes in insolation.

## 5.2. Precession-controlled variation of sources of organic matter

### 5.2.1. Influence of preservation, terrestrial input, and productivity on TOC fluctuations

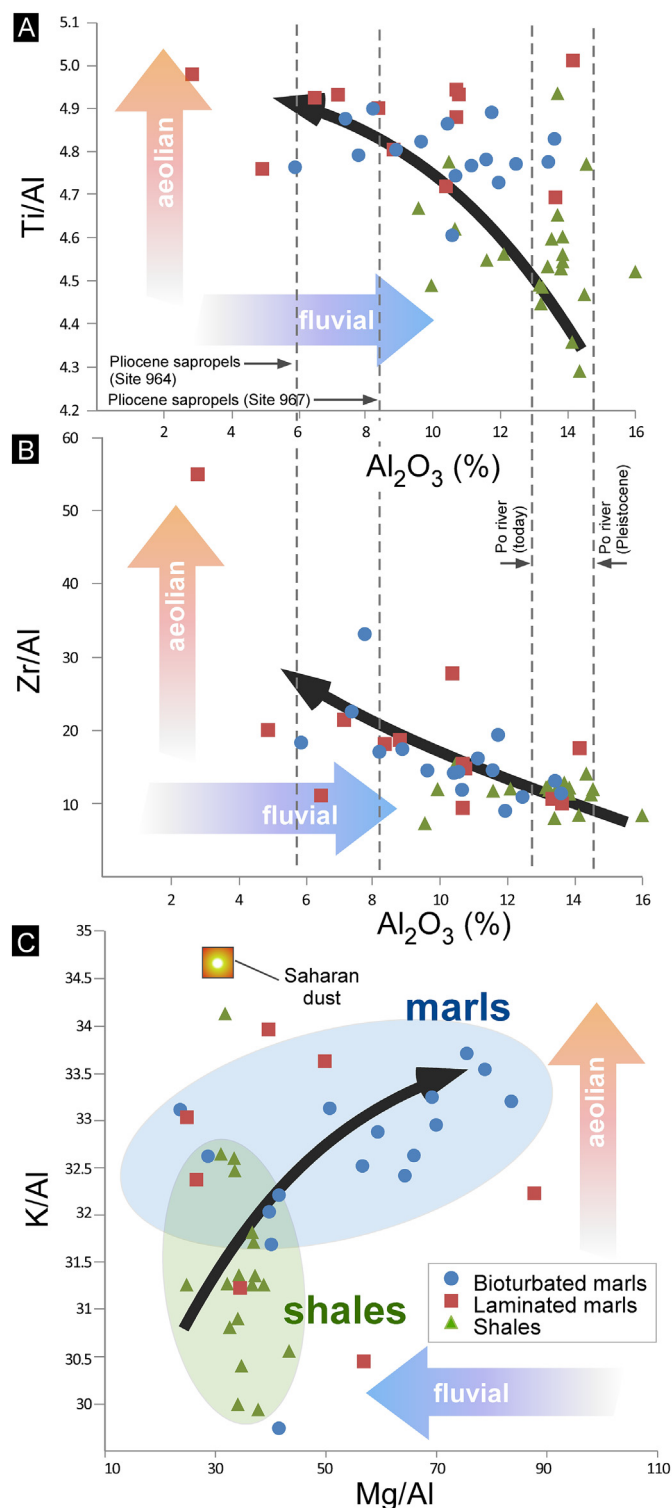
The TOC content of sediments is a function of the flux of organic carbon from both terrestrial and aquatic sources and preservation, with the latter controlled by the rate of oxidation in the water column and the seafloor (Calvert and Pedersen, 2007; Schoepfer et al., 2015).

Aerobic bacterial respiration is the most efficient pathway of organic carbon remineralization (Bernier, 1984). Oxygen depletion in bottom waters consequently favors the preservation of organic carbon, resulting in high TOC contents even when the flux of organic carbon is low (Van Os et al., 1994; Nijenhuis and De Lange, 2000; Rohling et al., 2015). In addition, preservation is favored by high sedimentation rates, decreasing the residence time of sediments at the seafloor and consequently reducing their exposure to oxygen (e.g., Schoepfer et al., 2015). Because the average sedimentation rate, obtained by dividing the thickness of each cycle by its duration (approximately 20 ka), remained almost constant across the onset of the MSC in the Pollenzo section (15 cm/kyr; Natalicchio et al., 2017), the high TOC contents of the shales must have been caused by other factors.

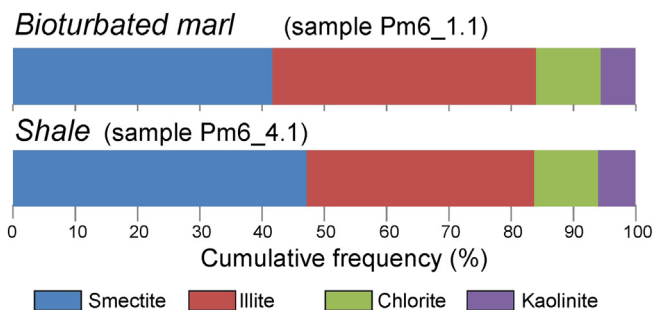
Changes in TOC contents follow lithological cyclicity with higher contents in shales (mean value of 2.0%) than in bioturbated marls (1.4%), although higher contents were observed in the laminated marls of cycles Pm6, Pm7, and especially Pg1 (up to 3.3%). TOC enrichment coincides with evidence of bottom water oxygen depletion, such as lamination, absence of bioturbation and of benthic foraminifers, as well as high pyrite contents. These observations suggest that reducing conditions at the seafloor favored organic carbon preservation. However, the positive covariation of TOC contents with the terrestrial long chain  $n$ -alkanes and the Ba/Al profile, the latter reflecting primary productivity (see below), suggests that organic carbon accumulation was a function of the combined effects of (1) variations in marine productivity, (2) input of terrestrial organic matter, and (3) enhanced preservation. Overall, the excellent correlation of TOC with lithology and the element-based paleoclimatic proxies (see above) strongly suggests that the supply of organic carbon was controlled by precession as documented for many pre-MSC sequences (cf. Nijenhuis et al., 1996; Schenau et al., 1999; Vazquez et al., 2000; Mayser et al., 2017) and younger Pliocene and Pleistocene sapropelitic sequences (cf. Rohling et al., 2015).

### 5.2.2. The supply of terrestrial organic matter: fluvial versus aeolian transport

Long chain  $n$ -alkanes are common constituents of the epicuticular waxes of terrestrial higher plants and for this reason are used as proxies of terrestrial organic matter input (e.g., Eglinton and Hamilton, 1963; Diefendorf et al., 2011). Their water insolubility and resistance to biodegradation makes these molecular fossils excellent recorders of climate-controlled change in terrestrial vegetation and input from the continent (e.g., Schefuß et al., 2003; Pancost and Boot, 2004). In the



**Fig. 10.** Plots of the Ti/Al (A) and Zr/Al ratios (B) versus total  $\text{Al}_2\text{O}_3$  contents in the studied Messinian samples and comparison with chemical compositions of Pliocene sapropels (Wehausen and Brumsack, 1998) and Pleistocene to recent Po River sediments (Amorosi et al., 2002). The  $\text{Al}_2\text{O}_3$  contents of the Pollenzo shales (green triangles) plot in the field of Po river sediments. C) Plot of K/Al and Mg/Al ratios. Samples with very high Mg/Al ratios ( $> 100$ ) from cycles Pm7 and Pg1 are excluded because of the presence of dolomite. Saharan dust composition is from Wehausen and Brumsack (1998). The black arrows indicate a trend of increased aeolian input. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 11.** Clay mineral compositions and relative abundance of shales (sample Pm6\_4.1) and bioturbated marls (sample Pm6\_1.1).

Pollenzo section, the abundance of long chain *n*-alkanes increases in the upper part of the section, with maximum contents in the MSC cycles (Pm6–Pm7; Fig. 7). This trend reflects an increased input of terrestrial organic matter during the first phase of the MSC. Long-chain *n*-alkanes reveal a cyclic pattern and a negative covariation with element/Al ratios, but a positive correlation with the total Al content. Taken together, these observations suggest that wet phases (low Ti/Al ratio) during insolation maxima – represented by shales – were characterized by maximum influx of terrestrial organic matter mainly supplied by rivers. Such covariation is particularly pronounced in the MSC part of the section (e.g., cycle Pm6; Figs. 6, 7). During arid phases (high Ti/Al ratio) at times of insolation minima – represented by bioturbated and laminated marls – influx of terrestrial organic matter from rivers was reduced due to the advent of more arid condition dominated by aeolian transport, which supplied a limited amount of organic matter.

### 5.2.3. Climate controlled variations of the source of terrestrial organic matter

The average chain length (ACL) of *n*-alkanes, the  $n\text{-C}_{31}/(n\text{-C}_{29} + n\text{-C}_{31})$ , and the compound-specific carbon isotope compositions of *n*-alkanes can be used to reconstruct the type of vegetation from which they were produced (e.g., Eglinton and Hamilton, 1963; Pancost and Boot, 2004; Diefendorf and Freimuth, 2017). Fluctuations among these proxies can be caused by changing contributions of plant species with different photosynthetic pathways ( $\text{C}_3$  and  $\text{C}_4$ ) to the pool of terrestrial organic matter (Castaneda et al., 2007), which is controlled by climate. It has been demonstrated that  $\text{C}_3$  plants, which use the Calvin-Benson cycle and prefer colder and more humid climate, tend to produce shorter *n*-alkane chains, resulting in low ACL and  $n\text{-C}_{31}/(n\text{-C}_{29} + n\text{-C}_{31})$  ratios (e.g., Rommerskirchen et al., 2006; Shepherd and Griffiths, 2006; Bush and McInerney, 2013, 2015), than  $\text{C}_4$  plants. The latter use the Hatch-Slack cycle and are better adapted to more arid and warmer conditions (e.g., Schefuß et al., 2003; Ortiz et al., 2013). In addition, the compound specific carbon isotopes ( $\delta^{13}\text{C}$ ) of *n*-alkanes derived from  $\text{C}_3$  plant waxes generally show more negative  $\delta^{13}\text{C}$  values ( $-38\text{‰}$  to  $-32\text{‰}$ ) than those of  $\text{C}_4$  plants ( $-25\text{‰}$  to  $-18\text{‰}$ ; Collister et al., 1994; Naafs et al., 2012). In the Pollenzo section the slight decrease of the ACL, of the  $n\text{-C}_{31}/(n\text{-C}_{29} + n\text{-C}_{31})$  ratio and of the  $\delta^{13}\text{C}$  values ( $\sim 4\text{‰}$  for  $\text{C}_{29}$  and  $\sim 7\text{‰}$  for  $\text{C}_{31-33}$ ) across the MSC onset (up to cycle Pm6) is negatively correlated with the progressive increase of content of terrestrial organic matter (Fig. 7). These trends are consistent with  $\text{C}_3$ -dominated vegetation, possibly reflecting an increase of humidity during the first phases of the MSC. In contrast, the increase of the *n*-alkane ratios (ACL and  $n\text{-C}_{31}/(n\text{-C}_{29} + n\text{-C}_{31})$ ) and the  $\delta^{13}\text{C}$  enrichment ( $\delta^{13}\text{C}$  shift  $\sim +4\text{‰}$ ) observed from cycle Pm7 upward suggests the establishment of dryer conditions (e.g., Eley and Hren, 2018) responsible for a vegetation change. This change is reflected by higher proportions of  $\text{C}_3$  plants adapted to more arid conditions and/or an increased contribution of arid-prone  $\text{C}_4$  plants (e.g., Diefendorf et al., 2011; Mayser et al., 2017).

The closer inspection of the *n*-alkanes ratios and isotopic



composition at the scale of the single lithological cycles reveals that shales yield values at the higher end (Figs. 7, 9), which is surprising. These values suggest greater contributions of  $C_4$  plants (or of  $^{13}C$ -enriched  $C_3$  plants), in contrast to the notion that shales were formed during more humid periods. This inconsistency can be explained considering the CPI index, which reflects the state of degradation and source of terrestrial organic matter (e.g., Bray and Evans, 1961; Schefuß et al., 2003). In general, the high CPI values observed for the majority of samples (~5 to 9) indicate good preservation and freshness of terrestrial organic matter supplied by higher plants (Jeng, 2006). Nevertheless, CPI shows significant fluctuation with lower values in the shales (as low as 2–3) and higher values in the bioturbated and laminated marls (as high as 8–9). Being out of phase with the  $n$ -alkane profile (Fig. 7), the lower CPI values of shales possibly reflect enhanced contribution of altered, mature terrestrial organic matter, recycled from older sediments (cf. Cortina et al., 2016). Therefore, the paleoclimate reconstructions based on  $n$ -alkane ratios and compound specific  $\delta^{13}C$  values from shales (Fig. 9) may be seriously biased. Such bias is apparently not affecting the bioturbated and laminated marls with their higher CPI values, reflecting fresher terrestrial organic matter mostly sourced from coeval plants growing close to the basin margins (Cortina et al., 2016).

#### 5.2.4. Marine primary productivity: the Ba/Al profile

The Ba content of sediments is used as an indicator of marine primary productivity based on the excellent correlation of organic carbon and Ba in sediments of modern oceans (e.g., Cardinal et al., 2005; Paytan and Griffith, 2007). Barium is closely associated with organic material during settling and is subsequently delivered as barite ( $BaSO_4$ ) to the seafloor (Calvert and Pedersen, 2007; Schoepfer et al., 2015). In the Pollenzo section, the Ba/Al profile shows a cyclic pattern (Fig. 6), revealing a negative covariation with the abundance of major elements (e.g., Si, K, Mg; see above) and a positive correlation with the TOC and the content of terrestrial lipids (with remarkable exceptions for the filament-bearing laminated marls of cycles Pm6, Pm 7 and Pg1; see below). These patterns indicate that marine primary productivity was increased during the deposition of the smectite-rich shales at times of insolation maxima, associated with the increased input of terrestrial lipids by enhanced riverine runoff. Probably, enhanced riverine runoff was responsible for an increased nutrient input into the basin, which caused eutrophication of the upper water column (cf. Friedrich et al., 2014). The facts that (1) shales contain abundant fecal pellets and clay rich aggregates with altered diatom frustules – both common components of marine “snow” forming in the upper oxygenated layers during episodes of enhanced productivity (Alldredge and Silver, 1988; Dela Pierre et al., 2014) – and (2) planktic foraminifer assemblages with abundant eutrophic taxa typify pre-MSD cycles (Lozar et al., 2018)

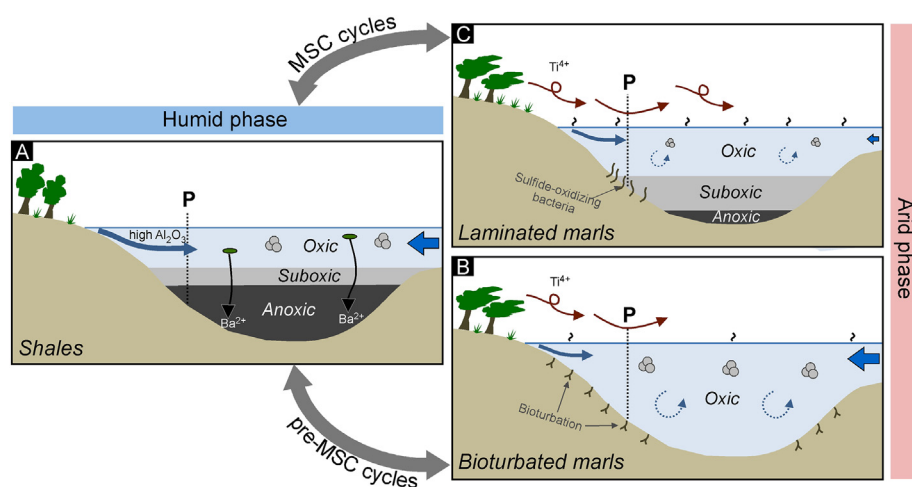
agree with such an interpretation.

The Ba profile could have been altered by post-depositional loss of accumulated barite in anoxic sediments. Barite tends to dissolve when exposed to anoxic pore waters from which sulfate is removed by intense bacterial sulfate reduction (e.g., Schoepfer et al., 2015). Oxygen-depleted bottom conditions during the deposition of the shales are suggested by the fine lamination of sediments and the absence of bioturbation. In addition, high contents of pyrite framboids agree with formerly pronounced bacterial sulfate reduction in the studied sediments. However, the Gaussian-shaped Ba/Al profile and the symmetrical Ba peaks strongly suggest that Ba distribution reflects changes in paleoproductivity (cf. Wehausen and Brumsack, 1999). Sulfate reduction was apparently not sufficient to decrease pore water sulfate concentration to the extent necessary for barite dissolution, possibly because sulfate was continuously replenished by seawater (e.g., Martinez-Ruiz et al., 2000). This interpretation agrees with the continuous occurrence of marine fossils (foraminifers, calcareous plankton, diatoms, fishes; Sturani, 1973; Violanti et al., 2013; Lozar et al., 2018), indicating a connection of the marginal basin to an open marine water body (Dela Pierre et al., 2014, 2015; Natalicchio et al., 2014), allowing for the supply of dissolved sulfate required for barite preservation.

Interestingly, no positive correlation exists between the Ba/Al ratio and the TOC contents in the filament bearing marls of cycles Pm6, Pm7, and Pg1. In these sediments, the high TOC contents (as high as 3%) are not associated with a parallel increase of the Ba/Al ratio, whereas the terrestrial lipid abundance remains constant or even decreases in cycle Pg1. This observation implies that these high TOC contents reflect a source of organic carbon other than terrestrial organic matter or marine primary productivity in the euphotic zone. A possible source includes a contribution from chemoautotrophy, which may agree with the sharp increase of archaeal communities above the MSC onset (Natalicchio et al., 2017) and with the interpretation of the super-abundant filamentous fossils as chemotrophic sulfide-oxidizing bacteria (Dela Pierre et al., 2012, 2014). In modern settings, mats of these bacteria are characterized by high rates of organic carbon accumulation from chemoautotrophy, adding to primary production by photoautotrophy in surface waters (Taylor et al., 2001; Jessen et al., 2016).

#### 5.3. Sedimentary response to astronomical forcing across the onset of the MSC

The Messinian organic-rich shales of the Pollenzo section show striking geochemical similarities with the more extensively studied Mediterranean Pliocene and Pleistocene sapropels (cf. Emeis et al., 2000; Rohling et al., 2015), suggesting that a single mechanism – enhanced riverine runoff with an increased supply of terrestrial organic matter and nutrients during insolation maxima – led to increased



**Fig. 12.** Sketch showing the climate-controlled paleoenvironmental changes affecting the studied marginal Mediterranean basin across the MSC onset (see text for explanations). A) Shale deposition during humid phases at precession minima (insolation maxima) before and after the MSC onset. B), C) Deposition of bioturbated marls (B) and laminated marls (C) during arid phases at precession maxima (insolation minima). Blue arrows indicate freshwater (thin arrow) and seawater (thick arrow) inputs. Blue dashed arrows indicate water mixing. Brown arrows indicate aeolian transport. P: Pollenzo section. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

productivity in the Mediterranean during the late Neogene (e.g., Nijenhuis et al., 1996; Negri et al., 1999; Schenau et al., 1999). Increased runoff resulted in water column stratification and bottom anoxia, which enhanced preservation of organic carbon (Fig. 12A). However, unlike the Mediterranean sapropels, the source of freshwater in the study area was not the Nile but rivers draining the uplifting Alpine chain. Our data support the notion that during the Late Miocene the Piedmont Basin was influenced by precessional-driven changes in the intensity of the North Atlantic Storm track (Kutzbach et al., 2014) and/or net convective precipitations over the Mediterranean Sea (Bosmans et al., 2015). Climate simulations suggest that both these mechanisms are able to supply an extra freshwater budget to the Northern Mediterranean at insolation maxima, in phase with the African monsoon (Meijer and Tuenter, 2007; Toucanne et al., 2015).

Although the organic-rich shales show similar geochemical and sedimentological patterns throughout most of the Pollenzo section, a change is observed across the MSC onset in the sediments reflecting the arid part of the precessional cycle. Bioturbated marls with low contents of TOC, terrestrial lipids, and Ba occur before the MSC onset (cycles Pm3 and Pm4) and in the earliest part of the MSC (cycle Pm5). In contrast, laminated and filament-bearing marls with high TOC contents (but low Ba contents) are observed in the two cycles above the MSC onset (Pm6 and Pm7) and in cycle Pg1, just below the first gypsum bed. This change possibly reflects variations in bottom water redox conditions, which may have been triggered by changes in the climatic or physiographic conditions of the basin after the onset of the MSC at times of insolation minima (Fig. 12B). Intense bioturbation of marls points to oxygenated bottom water conditions, which are best explained by low freshwater inflow in accordance with the reduced input of terrestrial lipids and decreased productivity as indicated by low Ba contents. These conditions favored mixing of the water column and flow of oxygen-rich waters to greater depth (e.g., Sierro et al., 2003; Friedrich et al., 2014). High bottom water oxygenation correspondingly lowered the preservation potential of organic carbon, which together with the reduced primary productivity and reduced supply of terrestrial organic matter resulted in low TOC contents.

In contrast, the massive occurrence of filamentous microfossils assigned to colorless sulfide-oxidizing bacteria in the laminated marls (Dela Pierre et al., 2012, 2014, 2015) is in accord with hypoxic bottom waters after the MSC onset (Fig. 12C). A comparison with modern settings indicates that these bacteria form dense microbial mats on the seafloor under variable hypoxic conditions (Schulz and Jørgensen, 2001; Musmann et al., 2003). Growth of chemotrophic sulfide-oxidizing bacteria is particularly favored by steep gradients of molecular oxygen or dissolved nitrate and hydrogen sulfide. Such conditions occur when the chemocline, separating oxygenated from anoxic waters below, impinges the sea bottom (Jessen et al., 2016). Likewise, water column stratification may even have occurred during insolation minima after the MSC onset, which is supported by the presence of tetrahymanol in the laminated marls (Natalicchio et al., 2017). This compound is found in bacterivorous ciliates (e.g., *Tetrahymena pyriformis*; Harvey and McManus, 1991), anoxygenic phototrophic bacteria (e.g., Eickhoff et al., 2013), and aerobic methanotrophic bacteria (Banta et al., 2015), all of which are abundant at chemoclines. Tetrahymanol (or its degradation product gammacerane) is consequently considered to be indicative of water-column stratification (Sinninghe Damsté et al., 1995).

In a marginal basin with limited water exchange with the global ocean, such as the Piedmont Basin during the Messinian (Sturani, 1973; Dela Pierre et al., 2011), intensification of water column stratification can result from steep thermal and salinity gradients, which are induced by warming of the upper water column or increased freshwater inflow from precipitation or riverine runoff (e.g., Friedrich et al., 2014). Warming is not indicated by current paleoclimate reconstructions, which rather suggest a cooling trend during the late Neogene (Herbert et al., 2016). Increased freshwater input is indicated by rising contents

of terrestrial molecular fossils from the pre-MSC bioturbated marls to the MSC filament-bearing laminated marls of cycle Pm6. The shift towards more  $^{13}\text{C}$ -depleted long chain *n*-alkanes and the shortening of their chain lengths suggests that a  $\text{C}_3$ -dominated terrestrial vegetation adapted to humid climate existed at that time. Paleobotanical data revealed strong climate gradients within the Mediterranean during the MSC, with the northern sub-basins (e.g., Piedmont and Vena del Gesso) characterized by moist climate and a positive hydrological budget (Bertini and Martinetto, 2011), in line with the findings of this study.

## 6. Conclusions

Trends in major and trace elements as well as molecular fossils allow assessing of the relationship between sedimentary cyclicity and precessional forcing in Messinian fossil-poor strata from the Piedmont Basin. In the studied Pollenzo section, organic-rich shales, which deposited during insolation maxima, remained unchanged across the onset of the MSC with respect to their geochemical and sedimentological characteristics. The higher organic carbon contents of shales compared to other lithologies resulted from increased primary productivity, interpreted to have been triggered by enhanced riverine runoff carrying nutrients into the basin. Moreover, preservation of organic carbon at times of shale deposition was favored by bottom water anoxia caused by water column stratification. The mode of formation of the Messinian organic-rich shales was apparently analogous to that inferred for their younger and more extensively studied Pliocene and Pleistocene counterparts (i.e., the Mediterranean sapropels), suggesting that similar mechanisms were responsible for the deposition of organic-rich sediments in the Mediterranean during the Neogene. Conversely, bioturbated and laminated marls deposited during dryer periods at insolation minima before and after the onset of the MSC. The trend from fully oxygenated conditions during marl deposition in pre-MSC times (bioturbated marls) to hypoxic conditions in the earliest MSC phases (laminated marls) is interpreted to reflect increasingly reducing bottom waters. Molecular fossil and element geochemical data suggest that water column stratification was intensified by the combined effects of persistent freshwater input and basin restriction heralding gypsum precipitation in this relatively deep basin. The used multi-proxy approach, combining sedimentological and petrographical analyses with element geochemistry and molecular fossils, has great potential for the reconstruction of climate-induced environmental change in sediments that are devoid of fossils. It may help to decipher the causes of severe environmental crises in Earth history.

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## References

- Algeo, T.J., Tribouillard, N., 2009. Environmental analysis of paleoceanographic systems based on molybdenum-uranium covariation. *Chem. Geol.* 268, 211–225.
- Aldredge, A.L., Silver, M.W., 1988. Direct observations of the mass flocculation of diatom blooms: characteristics, settling velocities, and formation of diatom aggregates. *Limnol. Oceanogr.* 20, 41–82.
- Amorosi, A., Centineo, M.C., Dinelli, E., Lucchini, F., Tateo, F., 2002. Geochemical and mineralogical variations as indicators of provenance changes in Late Quaternary deposits of SE Po Plain. *Sediment. Geol.* 151, 273–292.
- Babel, M., 2007. Depositional environments of a Salina type evaporite basin recorded in the Badenian gypsum facies in northern Carpathian Foredeep. In: Schreiber, B.C., Lugli, S., Babel, M. (Eds.), *Evaporites through Space and Time*. vol. 285. Geological Society of London, Special Publication, pp. 107–142.
- Banta, A.B., Wie, J.H., Welander, P.V., 2015. A distinct pathway for tetrahymanol synthesis in bacteria. *Proc. Natl. Acad. Sci. U. S. A.* 112, 13478–13483.
- Bellanca, A., Caruso, A., Ferruzza, G., Neri, R., Rouchy, J.M., Sprovieri, M., Blanc-Valleron, M.M., 2001. Transition from marine to hypersaline conditions in the Messinian Tripoli Formation from the marginal areas of the central Sicilian Basin. *Sediment. Geol.* 140, 87–105.
- Berner, R.A., 1984. Sedimentary pyrite formation: an update. *Geochim. Cosmochim. Acta* 48, 605–615.
- Bertini, A., Martinetto, E., 2011. Reconstruction of vegetation transects for the Messinian-Piacenzian of Italy by means of comparative analysis of pollen, leaf and carpological records. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 304, 230–246.
- Bigi, G., Cosentino, D., Parotto, M., Sartori, R., Scandone, P., 1990. Structural Model of Italy: Geodynamic Project. Consiglio Nazionale delle Ricerche (S.E.L.C.A., scale 1:500,000, sheet 1).
- Birgel, D., Thiel, V., Hinrichs, K.-U., Elvert, M., Campbell, K.A., Reitner, J., Farmer, J.D., Peckmann, J., 2006. Lipid biomarker patterns of methane-seep microbialites from the Mesozoic convergent margin of California. *Org. Geochem.* 37, 1289–1302.
- Boldrin, A., Bortoluzzi, G., Frascari, F., Guerzoni, S., Rabitti, S., 1988. Recent deposits and suspended sediments off the Po della Pila (Po River, main mouth), Italy. *Mar. Geol.* 79, 159–170.
- Bosmans, J.H.C., Drijfhout, S.S., Tuentner, E., Hilgen, F.J., Lourens, L.J., Rohling, E.J., 2015. Precession and obliquity forcing of the freshwater budget over the Mediterranean. *Quat. Sci. Rev.* 123, 16–30.
- Bray, E.E., Evans, E.D., 1961. Distribution of normal-paraffins as a clue to recognition of source beds. *Geochim. Cosmochim. Acta* 22, 2–15.
- Brumsack, H.J., 2006. The trace metal content of recent organic carbon-rich sediments: implications for Cretaceous black shale formation. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 232, 344–361.
- Bush, R.T., McNerney, F.A., 2013. Leaf wax *n*-alkane distributions in and across modern plants: implications for paleoecology and chemotaxonomy. *Geochim. Cosmochim. Acta* 117, 161–179.
- Bush, R.T., McNerney, F.A., 2015. Influence of temperature and C<sub>4</sub> abundance on *n*-alkane chain length distributions across the Central USA. *Org. Geochem.* 79, 65–73.
- Calvert, S.E., Pedersen, T.F., 2007. Elemental proxies for paleoclimatic and paleoceanographic variability in marine sediments: interpretation and application. In: Hillaire-Marcel, C., De Vernal, A. (Eds.), *Proxies in Late Cenozoic Paleoclimatology*, Developments in Marine Geology. vol. 1. Elsevier, pp. 567–644.
- Capella, W., Matenco, L., Dmitrieva, E., Roest, W.M.J., Hessels, S., Hssain, M., Chakor-Alami, A., Sierro, F.J., Krijgsman, W., 2016. Thick-skinned tectonics closing the Rifian Corridor. *Tectonophysics* 710–711, 249–265.
- Cardinal, D., Savoye, N., Trull, T.W., André, L., Kopczynska, E.E., Dehairs, F., 2005. Variations of carbon remineralisation in the Southern Ocean illustrated by the Ba<sub>ss</sub> proxy. *Deep-Sea Research I* 52, 355–370.
- Carrapa, B., Garcia-Castellanos, D., 2005. Western Alpine back-thrusting as subsidence mechanism in the Tertiary Piedmont Basin (western Po Plain, NW Italy). *Tectonophysics* 406, 197–212.
- Castaneda, I.S., Werne, J.P., Johnson, T.C., 2007. Wet and arid phases in the southeast African tropics since the Last Glacial Maximum. *Geology* 35, 823–826.
- Cita, M.B., Wright, R.C., Ryan, W.B.F., Longinelli, A., 1978. Messinian paleoenvironments. In: Hsü, K.J., Montadert, L. (Eds.), *Initial Reports of the Deep Sea Drilling Project 42*. U.S. Government Printing Office, Washington D.C., pp. 1003–1035.
- Collister, J.W., Lichtfouse, E., Hieshima, G., Hayes, J.M., 1994. Partial resolution of sources of *n*-alkanes in the saline portion of the Parachute Creek Member, Green River Formation (Piceance Creek Basin, Colorado). *Org. Geochem.* 21, 645–659.
- Cortina, A., Grimalt, J.O., Rigual-Hernandez, A., Ballegeer, A.M., Martat, B., Sierro, F.J., Flores, J.A., 2016. The impact of ice-sheet dynamics in western Mediterranean environmental conditions during terminations: an approach based on terrestrial long chain *n*-alkanes deposited in the upper slope of the Gulf of Lions. *Chem. Geol.* 430, 21–33.
- De Lange, G.J., Krijgsman, W., 2010. Messinian salinity crisis: a novel unifying shallow gypsum/deep dolomite formation mechanism. *Mar. Geol.* 275, 273–277.
- Dela Pierre, F., Bernardi, E., Cavagna, S., Clari, P., Gennari, R., Irace, A., Lozar, F., Lugli, S., Manzi, V., Natalicchio, M., Roveri, M., Violanti, D., 2011. The record of the Messinian salinity crisis in the Tertiary Piedmont Basin (NW Italy): the Alba section revisited. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 310, 238–255.
- Dela Pierre, F., Clari, P., Bernardi, E., Natalicchio, M., Costa, E., Cavagna, S., Lozar, F., Lugli, S., Manzi, V., Roveri, M., Violanti, D., 2012. Messinian carbonate-rich beds of the Tertiary Piedmont Basin (NW Italy): microbially-mediated products straddling the onset of the salinity crisis. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 344–345, 78–93.
- Dela Pierre, F., Clari, P., Natalicchio, M., Ferrando, S., Giustetto, R., Lozar, F., Lugli, S., Manzi, V., Roveri, M., Violanti, D., 2014. Flocculent layers and bacterial mats in the mudstone interbeds of the primary lower Gypsum unit (Tertiary Piedmont basin, NW Italy): Archives of paleoenvironmental changes during the Messinian salinity crisis. *Mar. Geol.* 355, 71–87.
- Dela Pierre, F., Natalicchio, M., Ferrando, S., Giustetto, R., Birgel, D., Carnevale, G., Gier, S., Lozar, F., Marabello, D., Peckmann, J., 2015. Are the large filamentous microfossils preserved in Messinian gypsum colorless sulfide-oxidizing bacteria? *Geology* 43, 855–858.
- Diefendorf, A.F., Freimuth, E.J., 2017. Extracting the most from terrestrial plant-derived *n*-alkyl lipids and their carbon isotopes from the sedimentary record: a review. *Org. Geochem.* 103, 1–22.
- Diefendorf, A.F., Freeman, K.H., Wing, S.L., Graham, H.V., 2011. Production of *n*-alkyl lipids in living plants and implications for the geologic past. *Geochim. Cosmochim. Acta* 75, 7472–7485.
- Duggen, S., Hoernie, K., van de Bogaard, P., Rupke, L., Phipps Morgan, J., 2003. Deep roots of the Messinian salinity crisis. *Nature* 422, 602–606.
- Eglinton, G., Hamilton, R.J., 1963. The distribution of alkanes. In: Swain, T. (Ed.), *Chemical Plant Taxonomy*. Academic Press, London, pp. 187–217.
- Eglinton, G., Hamilton, R.J., 1967. Leaf epicuticular waxes. *Science* 156, 1322–1335.
- Ehrmann, W., Schmiedl, G., Beuscher, S., Krüger, S., 2017. Intensity of African humid periods estimated from Saharan dust fluxes. *PLoS One* 12, e0170989. <https://doi.org/10.1371/journal.pone.0170989>.
- Eickhoff, M., Birgel, D., Talbot, H.M., Peckmann, J., Kappler, A., 2013. Oxidation of Fe(II) leads to increased C-2 methylation of pentacyclic triterpenoids in the anoxygenic phototrophic bacterium *Rhodospseudomonas palustris* strain TIE-1. *Geobiology* 11, 268–278.
- Eley, Y.L., Hren, M.T., 2018. Reconstructing vapor pressure deficit from leaf wax lipid molecular distributions. *Sci. Rep.* 8, 3967.
- Emeis, K.C., Sakamoto, T., Wehausen, R., Brumsack, H.J., 2000. The sapropel record of the eastern Mediterranean Sea—results of Ocean Drilling Program Leg 160. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 158, 371–395.
- Flecker, R., Krijgsman, W., Capella, W., de Castro Martins, C., Dmitrieva, E., Mayser, J.P., Marzocchi, A., Modestou, S., Ochoa, D., Simon, D., Tulbure, M., van den Berg, B., van der Schee, M., de Lange, G., Ellam, R., Govers, R., Gutjahr, M., Hilgen, F., Kouwenhoven, T., Lofi, J., Meijer, P., Sierro, F.J., Bachiri, N., Barhoun, N., Alami, A.C., Chacon, B., Flores, J.A., Gregory, J., Howard, J., Lunt, D., Ochoa, M., Pancost, R., Vincent, S., Yousfi, M.Z., 2015. Evolution of the Late Miocene Mediterranean–Atlantic gateways and their impact on regional and global environmental change. *Earth Sci. Rev.* 150, 365–392.
- Foeken, J.P.T., Dunai, T.J., Bertotti, G., Andriessen, P.A.M., 2003. Late Miocene to present exhumation in the Ligurian Alps (southwest Alps) with evidence for accelerated denudation during the Messinian salinity crisis. *Geology* 31, 707–800.
- Foucault, A., Mélières, F., 2000. Palaeoclimatic cyclicity in Central Mediterranean Pliocene sediments: the mineralogical signal. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 158, 311–323.
- Friedrich, J., Janssen, F., Aleynik, D., Bange, H.W., Boltacheva, N., Çagatay, M.N., Dale, A.W., Etiope, G., Erdem, Z., Geraga, M., Gilli, A., Gomoio, M.T., Hall, P.O.J., Hansson, D., He, Y., Holtappels, M., Kirf, M.K., Kononets, M., Kononov, S., Lichtschlag, A., Livingstone, D.M., Marinaro, G., Mazlumyan, S., Naeher, S., North, R.P., Papatheodorou, G., Pfannkuche, O., Prien, R., Rehder, G., Schubert, C.J., Soltwedel, T., Sommer, S., Stahl, H., Stanev, E.V., Teaca, A., Tengberg, A., Waldmann, C., Wehrli, B., Wenzhöfer, F., 2014. Investigating hypoxia in aquatic environments: diverse approaches to addressing a complex phenomenon. *Biogeosciences* 11, 1215–1259.
- García-Castellanos, D., Villaseñor, A., 2011. Messinian salinity crisis regulated by competing tectonics and erosion at the Gibraltar arc. *Nature* 480, 359–363.
- Gennari, R., Manzi, V., Angeletti, L., Bertini, A., Biffi, U., Ceregato, A., Faranda, C., Gliozzi, E., Lugli, S., Menichetti, E., Rosso, A., Roveri, M., Taviani, M., 2013. A shallow water record of the onset of the Messinian salinity crisis in the Adriatic foredeep (Legnagnone section, Northern Apennines). *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 386, 145–164.
- Gennari, R., Lozar, F., Turco, E., Dela Pierre, F., Manzi, V., Natalicchio, M., Lugli, S., Roveri, M., Schreiber, B.C., Taviani, M., 2018. Integrated stratigraphy and paleoceanographic evolution of the pre-evaporitic phase of the Messinian salinity crisis in the Eastern Mediterranean as recorded in the Tokhni section (Cyprus island). *Newsl. Stratigr.* 51 (1), 33–55.
- Gladstone, R., Flecker, R., Valdes, P., Lunt, D., Markwick, P., 2007. The Mediterranean hydrologic budget from a Late Miocene global climate simulation. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 251, 254–267.
- Hamann, Y., Ehrmann, W., Schmiedl, G., Kuhnt, T., 2009. Modern and late Quaternary clay mineral distribution in the area of the SE Mediterranean Sea. *Quat. Res.* 71, 453–464.
- Harvey, H.R., McManus, G.B., 1991. Marine ciliates as a widespread source of tetrahymanol and hopan-3 $\beta$ -ol in sediments. *Geochim. Cosmochim. Acta* 55, 3387–3390.
- Herbert, T.D., Lawrence, K.T., Tzanova, A., Peterson, L.C., Caballero-Gill, R., Kelly, C.S., 2016. Late Miocene global cooling and the rise of modern ecosystems. *Nat. Geosci.* 9, 843–847.
- Hilgen, F.J., Krijgsman, W., 1999. Cyclostratigraphy and astrochronology of the Tripoli diatomite formation (pre-evaporite Messinian, Sicily, Italy). *Terra Nova* 11, 16–22.
- Hilgen, F., Kuiper, K., Krijgsman, W., Snel, E., van der Laan, E., 2007. Astronomical tuning as the basis for high resolution chronostratigraphy: the intricate history of the Messinian Salinity Crisis. *Stratigraphy* 4, 231–238.
- Hsü, K., Montadert, L., Bernoulli, D., Cita, M.B., Erickson, A., Garrison, R.E., Kidd, R.B., Mélières, F., Müller, C., Wright, R., 1977. History of the Mediterranean salinity crisis. *Nature* 267, 399–403.
- Irace, A., Dela Pierre, F., Clari, P., 2005. “Normal” and “chaotic” deposits in the Messinian

- Gessoso-solfifera Fm. at the north eastern border of the Langhe domain (Tertiary Piedmont basin). *Boll. Soc. Geol. Ital.* 4, 77–85.
- Irace, A., Clemente, P., Natalicchio, M., Ossella, L., Trenkwalder, S., De Luca, D.A., Mosca, P., Piana, F., Polino, R., Violanti, D., 2010. Geologia e idrostratigrafia profonda della Pianura Padana occidentale: La Nuova Lito Firenze. 978-88-904554-0-7pp. 110.
- Jeng, W.L., 2006. Higher plant *n*-alkane average chain length as an indicator of petrogenic hydrocarbon contamination in marine sediments. *Mar. Chem.* 102, 242–251.
- Jessen, G.L., Lichtschlag, A., Struck, U., Boetius, A., Reese, B.K., Texas, A., Christl, M.U., 2016. Distribution and composition of thiotrophic mats in the hypoxic zone of the Black Sea (150–170 m water depth, Crimea margin). *Front. Microbiol.* 7, 1–14.
- Kouwenhoven, T.J., Morigi, C., Negri, A., Giunta, S., Krijgsman, W., Rouchy, J.M., 2006. Palaeoenvironmental evolution of the eastern Mediterranean during the Messinian: constraints from integrated microfossil data of the Pissouri Basin (Cyprus). *Mar. Micropaleontol.* 60, 17–44.
- Krijgsman, W., Hilgen, F., Raffi, I., Sierro, F., Wilson, D., 1999. Chronology, causes and progression of the Messinian salinity crisis. *Nature* 400, 652–655.
- Krijgsman, W., Fortuin, A.R., Hilgen, F.J., Roep, T.B., Sierro, F.J., 2001. Astrochronology for the Messinian Sorbas Basin (SE Spain) and orbital (precessional) forcing for evaporite cyclicity. *Sediment. Geol.* 140, 43–60.
- Kutzbach, J.E., Chen, G., Cheng, H., Edwards, R.L., Liu, Z., 2014. Potential role of winter rainfall in explaining increased moisture in the Mediterranean and Middle East during periods of maximum orbitally-forced insolation seasonality. *Clim. Dyn.* 42, 1079–1095.
- Laskar, J., Robutel, P., Joutel, F., Gastineau, M., Correia, A.C.M., Levrard, B., 2004. A long-term numerical solution for the insolation quantities of the Earth. *Astron. Astrophys.* 428, 261–285.
- Lindtke, J., Ziegenbalg, S.B., Brunner, B., Rouchy, J.M., Pierre, C., Peckmann, J., 2011. Authigenesis of native Sulphur and dolomite in a lacustrine evaporitic setting (Hellin basin, Late Miocene, SE Spain). *Geol. Mag.* 148, 655–669.
- Lozar, F., Violanti, D., Dela Pierre, F., Bernardi, E., Cavagna, S., Clari, P., Irace, A., Martinetto, E., Trenkwalder, S., 2010. Calcareous nannofossils and foraminifers herald the Messinian Salinity Crisis: the Pollenzo section (Alba, Cuneo; NW Italy). *Geobios* 43, 21–32.
- Lozar, F., Violanti, D., Bernardi, E., Dela Pierre, F., Natalicchio, M., 2018. Identifying the onset of the Messinian salinity crisis: a reassessment of the biochronostratigraphic tools (Piedmont Basin, NW Italy). *Newsl. Stratigr.* 51 (1), 11–31.
- Lugli, S., Manzi, V., Roveri, M., Schreiber, B.C., 2010. The Primary Lower Gypsum in the Mediterranean: a new facies interpretation for the first stage of the Messinian salinity crisis. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 297, 83–99.
- Manzi, V., Roveri, M., Gennari, R., Bertini, A., Biffi, U., Giunta, S., Maria, S., Lanci, L., Lugli, S., Negri, A., Riva, A., Edoardo, M., Taviani, M., 2007. The deep-water counterpart of the Messinian Lower Evaporites in the Apennine foredeep: the Fananello section (Northern Apennines, Italy). *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 251, 470–499.
- Manzi, V., Gennari, R., Hilgen, F., Krijgsman, W., Lugli, S., Roveri, M., Sierro, F.J., 2013. Age refinement of the Messinian salinity crisis onset in the Mediterranean. *Terra Nova* 25, 315–322.
- Manzi, V., Gennari, R., Lugli, S., Persico, D., Reghizzi, M., Roveri, M., Schreiber, B.C., Calvo, R., Gavrieli, I., Gvirtzman, Z., 2018. The onset of the Messinian salinity crisis in the deep Eastern Mediterranean basin. *Terra Nova* 30, 189–198.
- Martinez-Ruiz, F., Kastner, M., Paytan, A., Ortega-Huertas, M., Bernasconi, S.M., 2000. Geochemical evidence for enhanced productivity during S1 sapropel deposition in the eastern Mediterranean. *Paleoceanography* 15, 200–209.
- Marzocchi, A., Lunt, D.J., Flecker, R., Bradshaw, C.D., Farnsworth, A., Hilgen, F.J., 2015. Orbital control on late Miocene climate and the North African monsoon: in-sight from an ensemble of sub-precessional simulations. *Clim. Past* 11, 1271–1295.
- Mayser, J.P., Flecker, R., Marzocchi, A., Kouwenhoven, T.J., Lunt, D.J., Pancost, R.D., 2017. Precession driven changes in terrestrial organic matter input to the Eastern Mediterranean leading up to the Messinian Salinity Crisis. *Earth Planet. Sci. Lett.* 462, 199–211.
- Meijer, P.T., Tüent, E., 2007. The effect of precession-induced changes in the Mediterranean freshwater budget on circulation at shallow and intermediate depth. *J. Mar. Syst.* 68, 349–365.
- Modestou, S., Simon, D., Gutjahr, M., Marzocchi, A., Kowenhoven, T.J., Ellam, R.M., Flecker, R., 2017. Precessional variability of  $^{87}\text{Sr}/^{86}\text{Sr}$  in the late Miocene Sorbas Basin: an interdisciplinary study of drivers of interbasin exchange. *Paleoceanography* 32, 531–552.
- Möller, T., Schulz, H., Hamann, Y., Dellwig, O., Kucera, M., 2012. Sedimentology and geochemistry of an exceptionally preserved last interglacial S5 in the Levantine basin (Mediterranean Sea). *Mar. Geol.* 291–294, 34–48.
- Moore, D.M., Reynolds, R.C., 1997. X-ray Diffraction and the Identification and Analysis of Clay Minerals. Oxford University Press, New York (378 p).
- Mosca, P., Polino, R., Rogledi, S., Rossi, M., 2010. New data for the kinematic interpretation of the Alps–Apennines junction (Northwestern Italy). *Int. J. Earth Sci.* 99, 833–849.
- Mussmann, M., Schulz, H.N., Strotmann, B., Kyær, T., Nielsen, L.P., Rossellò-Mora, R.A., Amann, R.L., Jørgensen, B.B., 2003. Phylogeny and distribution of nitrate-storing *Beggiatoa* spp. in coastal marine sediments. *Environ. Microbiol.* 5, 523–533.
- Naafs, B.D.A., Heftner, J., Acton, G., Haug, G.H., Martínez-García, A., Pancost, R., Stein, R., 2012. Strengthening of North American dust sources during the late Pliocene (2.7 Ma). *Earth Planet. Sci. Lett.* 317, 8–19.
- Natalicchio, M., Dela Pierre, F., Lugli, S., Lowenstein, T.K., Feiner, S.J., Ferrando, S., Manzi, V., Roveri, M., Clari, P., 2014. Did late Miocene (Messinian) gypsum precipitate from evaporated marine brines? Insights from the Piedmont Basin (Italy). *Geology* 42, 179–182.
- Natalicchio, M., Birgel, D., Peckmann, J., Lozar, F., Carnevale, G., Liu, X., Hinrichs, K.-U., Dela Pierre, F., 2017. An archaeal biomarker record of paleoenvironmental change across the onset of the Messinian salinity crisis in the absence of evaporites (Piedmont Basin, Italy). *Org. Geochem.* 113, 242–253.
- Negri, A., Giunta, S., Hilgen, F., Krijgsman, W., Vai, G.B., 1999. Calcareous nannofossil biostratigraphy of the Monte del Casino section (Northern Apennines, Italy) and paleoceanographic conditions at the times of late Miocene sapropel formation. *Mar. Micropaleontol.* 36, 13–30.
- Nijenhuis, I.A., De Lange, G.J., 2000. Geochemical constraints on Pliocene sapropel formation in the eastern Mediterranean. *Mar. Geol.* 163, 41–63.
- Nijenhuis, I.A., Schenau, S.J., Van der Weijden, C.H., Hilgen, F.J., Lourens, L.J., Zachariasse, W.J., 1996. On the origin of upper Miocene sapropelites: a case study from the Faneromeni section, Crete, Greece. *Paleoceanography* 11, 633–645.
- Ortiz, J.E., Moreno, L., Trinidad, T., Vegas, J., Ruiz-Zapata, B., García-Cortés, Á., Galán, L., Pérez-González, A., 2013. A 220 ka palaeoenvironmental reconstruction of the Fuenllejo maar lake record (Central Spain) using biomarker analysis. *Org. Geochem.* 55, 85–97.
- Pancost, R.D., Boot, C.S., 2004. The palaeoclimatic utility of terrestrial biomarkers in marine sediments. *Mar. Chem.* 92, 239–261.
- Paytan, A., Griffith, E.M., 2007. Marine barite: recorder of variations in ocean export productivity. *Deep-Sea Research II* 54, 687–705.
- Perez-Folgado, M., Sierro, F.J., Barcena, M.A., Flores, J.A., Vazquez, A., Utrilla, R., Hilgen, F.J., Krijgsman, W., Filippelli, G.M., 2003. Western versus eastern Mediterranean palaeoceanographic response to astronomical forcing: a high-resolution microplankton study of precession-controlled sedimentary cycles during the Messinian. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 190, 317–334.
- Poynter, J., Eglinton, G., 1990. Molecular composition of three sediments from Hole 717C: the Bengal Fan. In: Cochran, J.R., Stow, D.A.V. (Eds.), *Proc. ODP, Sci. Results*. vol 116. pp. 155–161 College Station, TX (Ocean Drilling Program).
- Reghizzi, M., Gennari, R., Douville, E., Lugli, S., Manzi, V., Montagna, P., Roveri, M., Sierro, F.J., Taviani, M., 2017. Isotope stratigraphy ( $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ ) of the Sorbas basin (Betic Cordillera, Spain): paleoceanographic evolution across the onset of the Messinian salinity crisis, 2017. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 469, 60–73.
- Rohling, E.J., Marino, G., Grant, K.M., 2015. Mediterranean climate and oceanography and the periodic development of anoxic events (sapropels). *Earth-Sci. Rev.* 143, 62–97.
- Rommerskirchen, F., Eglinton, G., Dupont, L., Rullkötter, J., 2006. Glacial/interglacial changes in southern Africa: compound-specific  $\delta^{13}\text{C}$  land plant biomarker and pollen records from southeast Atlantic continental margin sediments. *Geochem. Geophys. Geosyst.* 7, Q08010.
- Rossi, M., 2017. Outcrop and seismic expression of stratigraphic patterns driven by accommodation and sediment supply turnarounds: Implications on the meaning and variability of unconformities in syn-orogenic basins. *Mar. Pet. Geol.* 87, 112–127.
- Rossi, M., Mosca, P., Polino, R., Biffi, U., 2009. New outcrop and subsurface data in the Tertiary Piedmont Basin (NW Italy): unconformity bounded stratigraphic units and their relationships with basin modification phases. *Riv. Ital. Paleontol. Stratigr.* 115, 305–335.
- Roveri, M., Lugli, S., Manzi, V., Schreiber, B.C., 2008. The Messinian Sicilian stratigraphy revisited: new insights for the Messinian salinity crisis. *Terra Nova* 20, 483–488.
- Roveri, M., Flecker, R., Krijgsman, W., Lofi, J., Lugli, S., Manzi, V., Sierro, F.J., Bertini, A., Camerlenghi, A., De Lange, G., Govers, R., Hilgen, F.J., Hübscher, C., Meijer, P.T., Stoica, M., 2014. The Messinian Salinity Crisis: past and future of a great challenge for marine sciences. *Mar. Geol.* 352, 25–58.
- Schefeuf, E., Ratemeyer, V., Stuut, J.B.W., Jansen, H.F., Sinninghe Damsté, J.S., 2003. Carbon isotope analyses on *n*-alkanes in dust from the lower atmosphere over the central eastern Atlantic. *Geochim. Cosmochim. Acta* 67, 1757–1767.
- Schenau, S.J., Antonarakou, A., Hilgen, F.J., Lourens, L.J., Nijenhuis, I.A., van der Weijden, C.H., Zachariasse, W.J., 1999. Organic-rich layers from Metochia section (Gavdos, Greece): evidence for a single mechanism of sapropel deposition during the past 10 My. *Mar. Geol.* 153, 117–135.
- Schnetger, B., 1992. Chemical composition of loess from a local and worldwide view. *Neues Jahrb. Mineral. Monatshefte* 1, 29–47.
- Schoepfer, S.-D., Shen, J., Wei, H., Tyson, R.W., Ingall, E., Algeo, T.J., 2015. Total organic carbon, organic phosphorous, and biogenic barium fluxes as proxies for paleo-marine productivity. *Earth Sci. Rev.* 149, 23–52.
- Schultz, L.G., 1964. Quantitative interpretation of mineralogical composition from X-ray and chemical data for the Pierre Shale. In: US Geological Survey Prof. Paper 391-C, Washington.
- Schulz, H.N., Jørgensen, B.B., 2001. Big bacteria. *Annu. Rev. Microbiol.* 55, 105–137.
- Shepherd, T., Griffiths, W.D., 2006. The effects of stress on plant cuticular waxes. *New Phytol.* 171, 469–499.
- Sierro, F.J., Hilgen, F.J., Krijgsman, W., Flores, J.A., 2001. The Abad composite (SE Spain): a Messinian reference section for the Mediterranean and the APTS. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 168, 141–169.
- Sierro, F.J., Flores, J.A., Frances, G., Vazquez, A., Utrilla, R., Zamarreno, I., Erlenkeuser, H., Barcena, M.A., 2003. Orbitally-controlled oscillations in planktic communities and cyclic changes in western Mediterranean hydrography during the Messinian. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 190, 289–316.
- Simon, D., Marzocchi, A., Flecker, R., Lunt, D.J., Hilgen, F.J., Meijer, P.T., 2017. Quantifying the Mediterranean freshwater budget throughout the late Miocene: new implications for sapropel formation and the Messinian salinity crisis. *Earth Planet. Sci. Lett.* 472, 25–37.
- Sinninghe Damsté, J.S., Kuypers, M.M.M., Schouten, S., Schulte, S., Rullkötter, J., 2003. The lycopene/ $\text{C}_{31}$  *n*-alkane ratio as a proxy to assess palaeoacidity during sediment deposition. *Earth Planet. Sci. Lett.* 209, 215–226.
- Sinninghe Damsté, J.S., Kenig, F., Koopmans, M.P., Köster, J., Schouten, S., Hayes, J.M.,



- de Leeuw, J.W., 1995. Evidence for gammacerane as an indicator of water column stratification. *Geochim. Cosmochim. Acta* 59, 1895–1900.
- Sturani, C., 1973. A fossil eel (*Anguilla* sp.) from the Messinian of Alba (Tertiary Piedmont Basin). Palaeoenvironmental and palaeogeographic implications. In: Drooger, C.W. (Ed.), *Messinian Events in the Mediterranean*. K. Nederl. Akad. Wetensch, Amsterdam, pp. 243–255.
- Taylor, G.T., Iabichella, M., Ho, T.Y., Scranton, M.I., Thunnell, R.C., Karger, M., Varela, R., 2001. Chemoautotrophy in the redox transition zone of the Cariaco Basin: a significant midwater source of organic carbon production. *Limnol. Oceanogr.* 46, 148–163.
- Tomadin, L., 2000. Sedimentary fluxes and different dispersion mechanisms of the clay sediments in the Adriatic Basin. *Rendiconti Lincei* 11, 161–174.
- Tomadin, L., Lenaz, R., 1989. Eolian dust over the Mediterranean and their contribution to the present sedimentation. In: Leinen, M., Sarnthein, M. (Eds.), *Paleoclimatology and Paleometeorology: Modern and Past Patterns of Global Atmospheric Transport*. Kluwer, Dordrecht, pp. 267–282.
- Tomadin, L., Lenaz, R., Landuzzi, V., Mazzucotelli, A., Vannucci, R., 1984. Wind-blown dusts over the Central Mediterranean. *Oceanol. Acta* 7, 13–23.
- Toucanne, S., Minto, C.M.A., Fontanier, C., Bassetti, M.A., Jorry, S.J., Jouet, G., 2015. Tracking rainfall in the northern Mediterranean borderlands during sapropel deposition. *Quat. Sci. Rev.* 129, 178–195.
- van der Laan, E., Hilgen, F.J., Lourens, L.J., de Kaenel, E., Gaboardi, S., Iaccarino, S., 2012. Astronomical forcing of Northwest African climate and glacial history during the late Messinian (6.5–5.5 Ma). *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 313, 107–126.
- Van Os, B.J.H., Lourens, L.J., Hilgen, F.J., De Lange, G.J., Beaufort, L., 1994. The formation of Pliocene sapropels and carbonate cycles in the Mediterranean: diagenesis, dilution and productivity. *Paleoceanography* 9, 601–617.
- Vazquez, A., Utrilla, R., Zamarreno, I., Sierro, F.J., Flores, J.A., Francés, G., Bàrcena, M.A., 2000. Precession-related sapropelites of the Messinian Sorbas Basin (South Spain): paleoenvironmental significance. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 158, 353–370.
- Violanti, D., Gallo, L.M., Rizzi, A., 2007. Foraminiferal assemblages of the Bric della Muda laminites (Nizza Monferrato, Piedmont): proxies of cyclic paleoenvironmental changes in the lower Messinian of North-Western Italy. *Geobios* 40, 281–290.
- Violanti, D., Lozar, F., Natalicchio, M., Dela Pierre, F., Bernardi, E., Clari, P., Cavagna, S., 2013. Stress-tolerant microfossils of a Messinian succession from the Northern Mediterranean basin (Pollenzo section, Piedmont, northwestern Italy). *Boll. Soc. Paleontol. Ital.* 52, 45–54.
- Wakeham, S.G., Amann, R., Freeman, K.H., Hopmans, E.C., Jørgensen, B.B., Putnam, I.F., Schouten, S., Sinninghe Damsté, J.S., Talbot, H.M., Woebken, D., 2007. Microbial ecology of the stratified water column of the Black Sea as revealed by a comprehensive biomarker study. *Org. Geochem.* 38, 2070–2097.
- Wehausen, R., Brumsack, H.J., 1998. The formation of Pliocene Mediterranean sapropels: constraints from high-resolution major and minor element studies. In: Robertson, A.H.F., Emeis, K.-C., Richter, C., Camerlenghi, A. (Eds.), *Proc. ODP, Sci. Results*, pp. 207–217. College Station, TX (Ocean Drilling Program).
- Wehausen, R., Brumsack, H.J., 1999. Cyclic variations in the chemical composition of eastern Mediterranean Pliocene sediments: a key for understanding sapropel formation. *Mar. Geol.* 153, 161–176.
- Wehausen, R., Brumsack, H.J., 2000. Chemical cycles in Pliocene sapropel-bearing and sapropel-barren eastern Mediterranean sediments. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 158, 325–352.
- Wilkin, R.T., Barnes, H.L., Brantley, S.L., 1996. The size and distribution of framboidal pyrite in modern sediments: an indicator of redox conditions. *Geochim. Cosmochim. Acta* 60, 3897–3912.
- Willet, S.D., Schlunneger, F., Picotti, V., 2006. Messinian climate change and erosional destruction of the central European Alps. *Geology* 34, 613–616.
- Zhao, Y., Colin, C., Liu, Z., Bonneau, L., Siani, G., 2016. Climate forcing of terrigenous sediment input to the Central Mediterranean Sea since the early Pleistocene. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 442, 23–35.